8-9098

# Final Report

## Fomi Project

April 1990

MICROMEDIA

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# TITLE: DEVELOPMENT OF A FIBER-OPTICS COUPLED FOURIER TRANSFORM NEAR-INFRARED SPECTROMETER (UP-B-7-025)

FINAL REPORT
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# RESUME

En novembre 1988, Les Laboratoires de recherche sur le charbon, situés à Devon, Alberta, une division du Ministère de l'Energie, Mines et Ressource Canada, ont octroyé à BOMEM Inc., dans le cadre d'un programme de développement du gouvernement fédéral, un contrat portant sur le développement d'un nouveau système utilisant la technologie de la spectroscopie proche infra-rouge par Transformée de Fourier.

L'objectif principal de ce projet était le développement d'un spectromètre proche infra-rouge ainsi que de certains accessoires d'échantillonnage. La particularité de ce système réside dans le fait que le spectromètre est relié par fibres optique aux accessoires, permettant ainsi d'échantillonner à distance les échantillons. Un objectif secondaire était de mesuré le contenu en eau dans une solution composée d'huile et d'eau.

Le spectromètre et ses accessoires serviront comme outils à l'élaboration d'un nouveau consortium dont le but sera de développer de nouvelles techniques d'analyse permettant d'améliorer le rendement et la qualité des produits des compagnies pétrolières canadiennes.

Le système fut livré à la fin du mois de février et installé au début de mars. Nous considérons que ce projet est un succès, car il nous a premis de trouver d'autres applications à nos produits tout en acquérant des nouvelles connaissances sur des technologies de pointe, telles les fibres optiques permettant l'échantillonnage à distance d'échantillons dans des environnements à risque élevé.

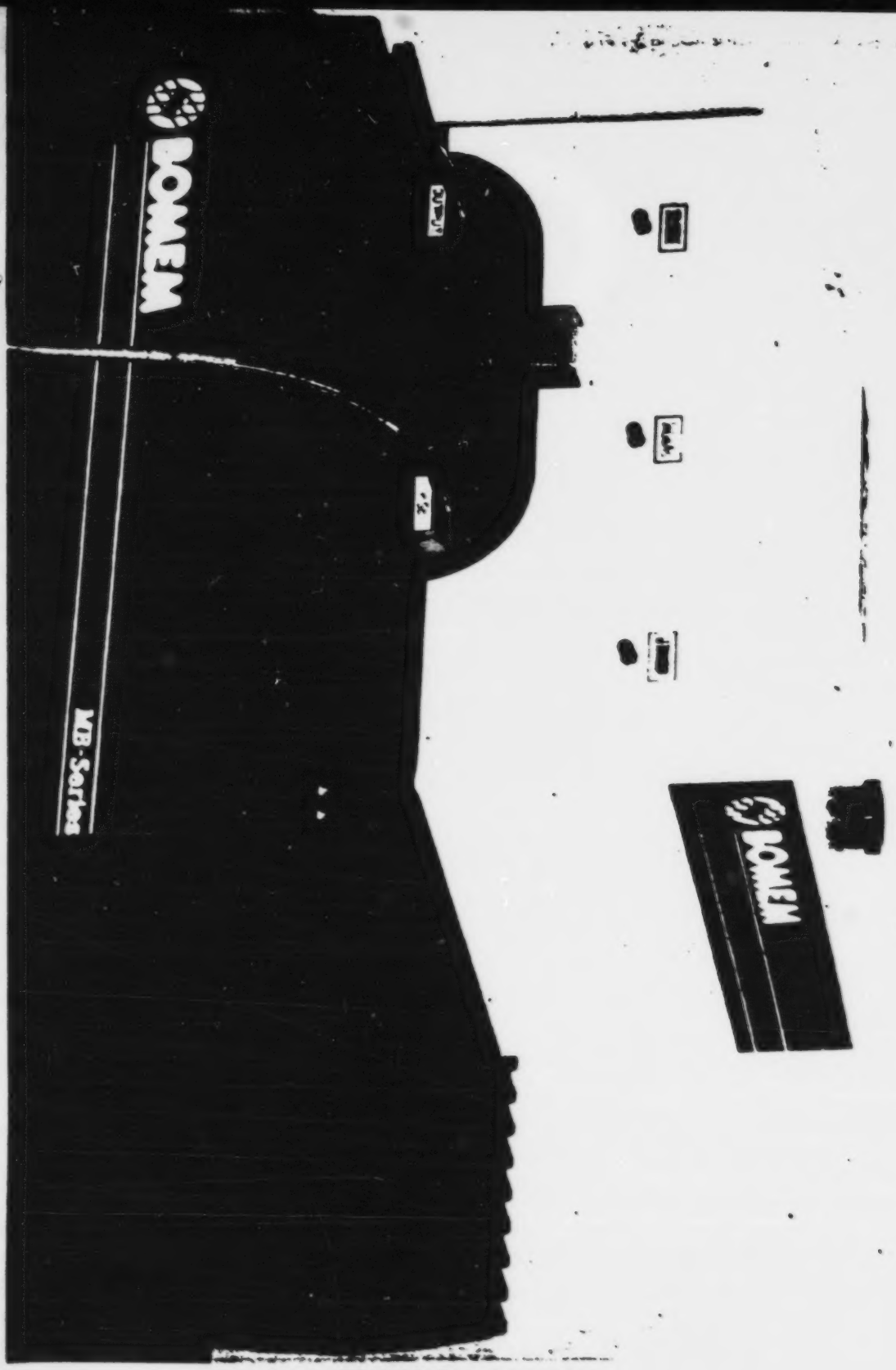
# SUMMARY

In November 1988, Energy, Mines and Resources Canada, CANMET CRL Division, and Bomem signed an agreement to develop a new FT-NIR system as part of the Program of the Federal Panel on Energy R&D (PERD).

The main objective of this contract was to develop a FT-NIR system and its accessories. All the accessories are coupled to the spectrometer by fiber optics which provide remote sampling. An auxiliary objective is to measure water content in oil/water emulsions.

The instrument and accessories developed in this project will be used to start a new consortium in order to generate new techniques in order to increase the efficiency and the quality of the Canadian petroleum companies.

The system was delivered at the end of February 1990 and installed at the beginning of March. We consider that this project was a great success and gave us the opportunity to find other applications for our product using fiber optics for remote sensing in hazardous environment.

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# 1. INTRODUCTION

This report describes the work that was done during the FOMI Project. In collaboration with Energy, Mines and Resources, CANMET CRL division, we have developed a new FT-NIR instrument, complete with Fiber Optics coupling and Fiber Optics coupled accessories. This main goal for which this instrument has been designed is to measure the water content of oil/water emulsion. This important problem, frequently encountered within the Canadian oil companies, can be efficiently handled using the precision and the flexibility given by a Fourier Transform Near Infrared spectrometer.

To reach our goals, we have used state-of-the-art technologies commercially available on the market. This project gave us the opportunity to acquire knowledge in special fields like fiber-optics and continuous monitoring process.

# 2. THE INSTRUMENT

This chapter describes the problems and solutions found in the development of an instrument designed to detect the water content of oil/water emulsions. The instrument is based on our Michelson Spectrometer; the interferometer, the source, the scanning speed and the coupling interface to the accessories were modified. We will briefly describe each modification that was made on the standard system, in order to upgrade it to a state-of-the-art FT-NIR Fiber Optics coupled spectrometer.

## 2.1. Principle

Several parts are included in a spectrometer:

- Source
- Interferometer
- Electronic control
- One or many detectors
- Sample area

The light from the source is modulated by the interferometer, then passes through a sample in which a few specific frequencies are absorbed and other are not affected. The light which goes through the sample is focussed on the detector, sampled, digitalised and transferred to the computer to be analyzed. This is a very simplified explanation of the function of a spectrometer. See Appendix A for the spectrometer general description.

We will describe the general modifications we made to the system in order to reach our objectives.

## 2.2. Source

The NIR region is closer to the visible region than the mid Infrared. We needed a high intensity source to be able to work with crude oil samples.

We replaced our Mid IR source (a globar) by a visible one. We selected a Quartz Halogen source provided with a long life time and not to high consumption of current to avoid excessive heat of the instrument and disturbance of the mechanical and optical components in the spectrometer. We designed a new holder for the source and modified the power supply corresponding to this new source.

## 2.3. The Interferometer

### 2.3.1. The Beamsplitter

The first requirement was to work in the NIR region (2000 $cm^{-1}$ to 14000 $cm^{-1}$).

We therefore designed a new beamsplitter in calcium fluoride CaF2 to replace our standard KBr beamsplitter. The new beamsplitter resulted in a modulation around 50% at 10000 $cm^{-1}$. This result is possible because the calcium fluoride is a very hard material providing better quality of the polishing, good flatness and better parallelism, compared to the standard KBr beamsplitter. See Appendix B for the beamsplitter general specifications.

### 2.3.2. The Retroreflectors (Corner Cubes)

In the NIR region the optical frequencies in the signal are much higher than in the Mid IR. This is why we need better accuracy.

In order not to attenuate the higher frequencies to much, we replaced the standard retroreflectors (5 arc second) by one provided with a precision of 0.5 arc second. The high level of modulation at 10000 $cm^{-1}$ we had was given by the combination of a good beamsplitter and a high precision retroreflector. See Appendix C for the retroreflectors general specifications.

## 2.4. Electronic control

### 2.4.1. The Over-sampling

To be able to work in the NIR Region, we had to gave to our instrument the power to sample two times faster.

Our instrument is using a HeNe laser to synchronize data acquisition. The principle of the interferometer is to use the laser fringes (interferences) produced by the movement of the two retroreflectors to spatially sample the signal at the detector. We use a laser for its reproducibility. For a Mid IR signal, we sample on the rising edge on one direction and on the falling edge on the other direction to be able to sample at the same point spatially. The frequency of the HeNe laser is 15798 $cm^{-1}$ and the Nyquist theorem tell us that the higher signal we can sample is the sampling frequency divided by two. For this reason we modified the sampling circuit to be able to sample on the rising and falling edge of each laser fringes. The resulting interferogram has twice more points in NIR compared to the Mid IR.

### 2.4.2. The scanning speed

In our standard Michelson product, we support two speeds optimized for the best detector performances. We have seen that in NIR we have twice the number of points in the interferogram compared to the Mid IR.

To support the higher transfer rate between the spectrometer and the computer for the system's optimal performances, we included a DSP board. This board provides two major advantages. First, we can use the high speed for fast detectors. Secondly, this board reduces the computation time of a spectra. It was designed using a special chip, especially intended for FFT calculation. The time required to calculate a FFT on interferogram at 2 $cm^{-1}$ is less than one second versus 45 seconds if a 286 computer is used to calculate the same FFT. See Appendix D for the DSP board general description.

## 2.5. Detectors.

In order to increase the detection sensitivity in the N.I.R region of the spectrum (a need expressed by Dr. Donini along the project), we have provided the system with more than one detector. Indeed we have added to the InSb detector three more detectors, which are:

-one room temperature Germanium detector;
-one room temperature Indium Gallium Arsenide detector;
-one room temperature Silicon detector.

Each detector comes complete with its matched variable gain preamplifier. The characteristics and Signal to Noise performances of each provided detector are listed in the following tables.

Figure 1 below also presents the spectral response curves of the four (4) detectors. Those spectral response curves were all plotted using the same X and Y scales.

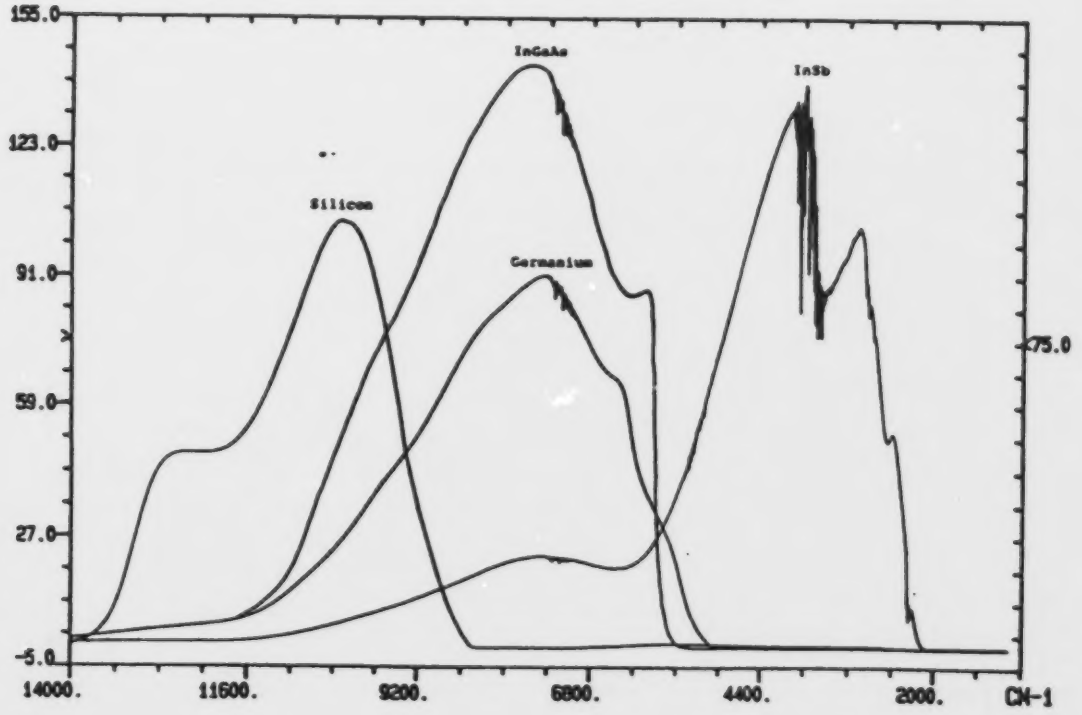



Figure 1 Spectral response curves of the detectors

Indium Antimonide detector (InSb).

-Operating temperature: 77 K (LN2 cooled);
-Detector size: 1.0 mm diameter;
-$D^*$greater than or equal to 1.0x1011 cm Hz1/2 W-1;
-Useful spectral range: 2100 to 8500 $cm^{-1}$ (see figure 2);
-Dewar hold time: from 8 to 12 hours;

Signal to Noise performances.
Tests performed:

1- Closed loop of 60 meters of ZrF Fiber (2x30 meters);
Fiber diameter=250 microns;
Fiber N.A.=0.2;
Preamplifier first stage feedback resistor=787 KOhms;
Preamplifier gain=2;
Spectral range=4250 to 4350 $cm^{-1}$;
Resolution=4 $cm^{-1}$;
Speed = 1.0 cm/sec optical;
The S/N ratio is an average of ten experiments and is a peak-to-peak value).

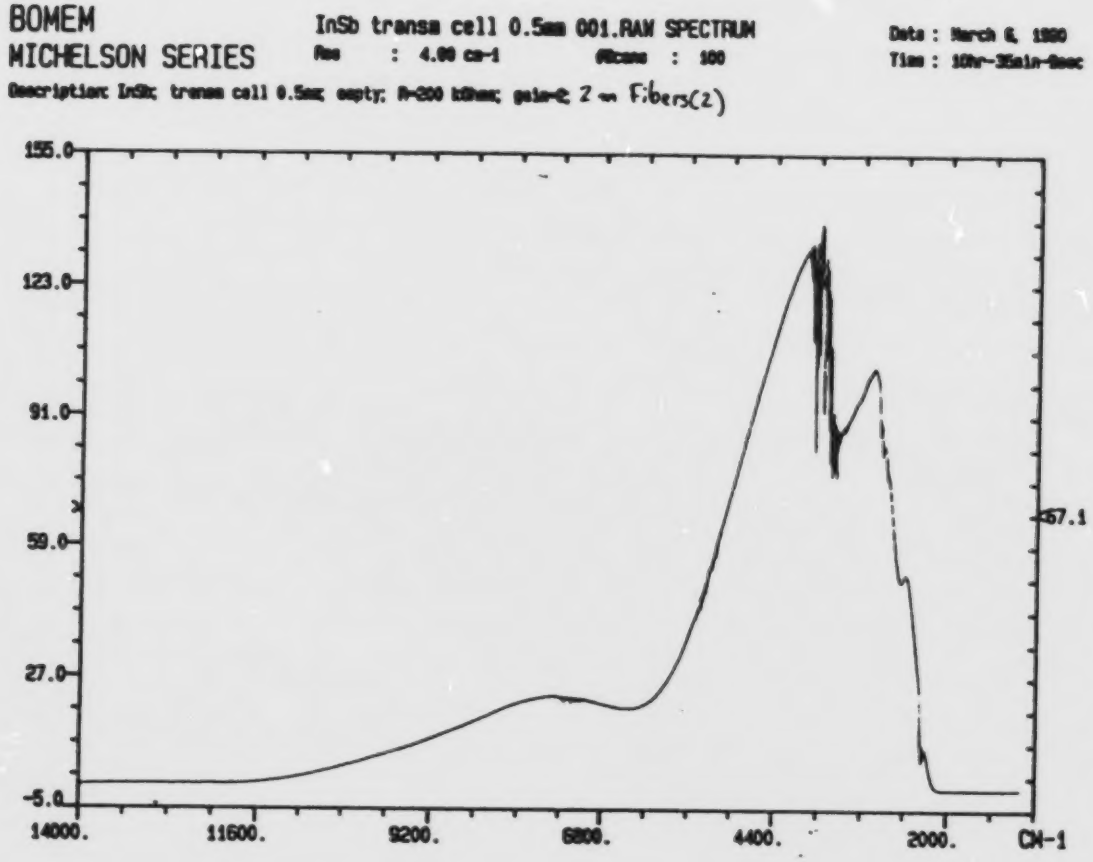
Results: 1 scan (≅1.5 seconds) : S/N = 330:1;
100 scans (≅2.5 minutes) : S/N = 3166:1;

2- 2x2 meters of ZrF Fiber + transmission cell;
Fiber diameter = 250 microns;
Fiber N.A. = 0.2;
Cell Windows: CaF2;
Window thickness: 3.6 mm (0.5 degree wedge);
Cell pathlength: 0.5 mm;
Cell was empty;
Preamplifier first stage feedback resistor=200 KOhms;
Preamplifier gain = 2;
Spectral range = 4250 to 4350 $cm^{-1}$;
Resolution = 4 $cm^{-1}$;
Speed = 1.0 cm/sec optical;
The S/N ratio is an average of ten experiments and is a peak-to-peak value).

Results: 1 scan (≅1.5 seconds) : S/N = 641:1;
100 scans (≅2.5 minutes) : S/N = 5584:1;

Table 1 InSb detector S/N performances

Figure 2 InSb spectral response curve



Germanium detector (Ge).

-Operating temperature: room temperature;
-Detector size: 1.0 mm diameter;
-$D^*$ greater than or equal to 3.0x1011 cm Hz1/2 W-1;
-Useful spectral range: 5500 to 10000 $cm^{-1}$ (see figure 3);

Signal to Noise performances.
Tests performed:

1- Closed loop of 60 meters of ZrF Fiber (2x30 meters);
Fiber diameter = 250 microns;
Fiber N.A. = 0.2;
Preamplifier first stage feedback resistor: 2.0 MOhms;
Preamplifier gain = 1;
Spectral range = 7550 to 7650 $cm^{-1}$;
Resolution = 4 $cm^{-1}$;
Speed = 1.0 cm/sec optical;
The S/N ratio is an average of ten experiments and is a peak-to-peak value).

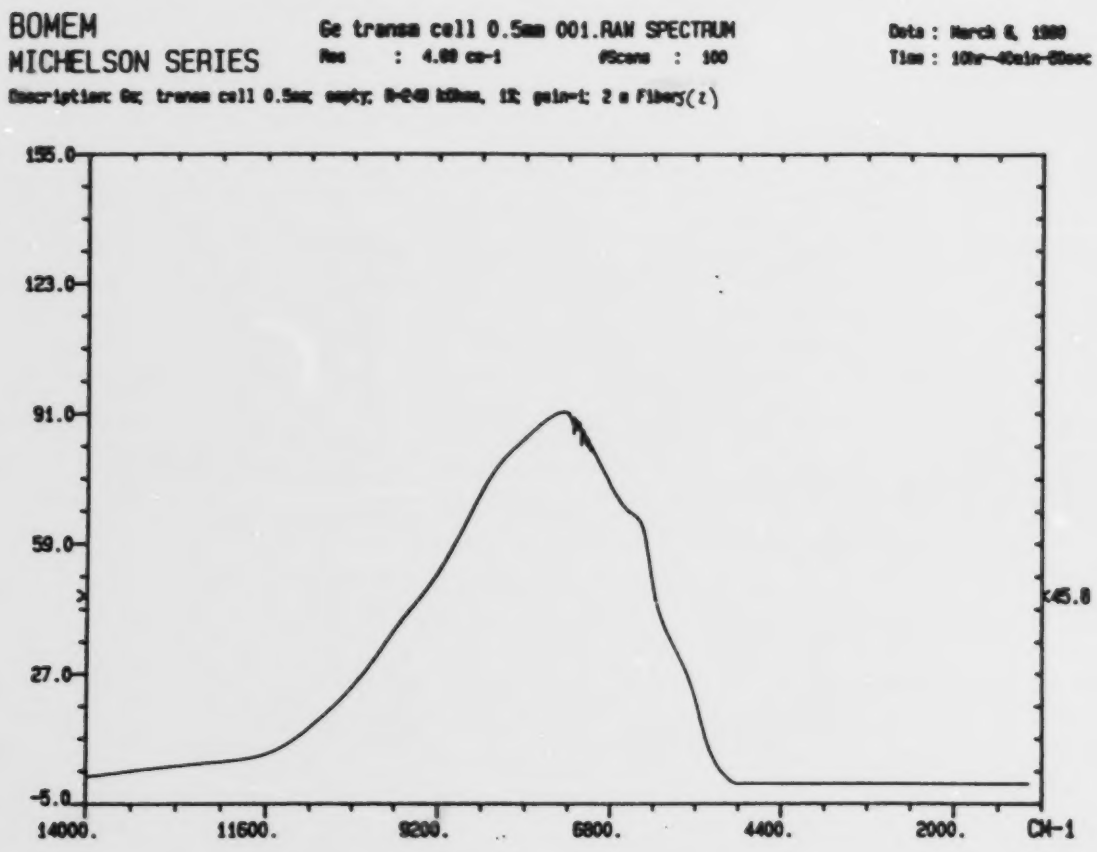
Results: 1 scan (≅ 1.5 seconds) : S/N = 191:1;
100 scans (≅2.5 minutes) : S/N = 2046:1;

2- 2x2 meters of ZrF Fiber + transmission cell;
Fiber diameter = 250 microns;
Fiber N.A. = 0.2;
Cell Windows: CaF2;
Window thickness: 3.6 mm (0.5 degree wedge);
Cell pathlength: 0.5 mm;
Cell was empty;
Preamplifier first stage feedback resistor = 249 KOhms;
Preamplifier gain = 1;
Spectral range = 4250 to 4350 $cm^{-1}$;
Resolution = 4 $cm^{-1}$;
Speed = 1.0 cm/sec optical;
The S/N ratio is an average of ten experiments and is a peak-to-peak value).

Results: 1 scan (≅ 1.5 seconds) : S/N = 621:1;
100 scans (≅2.5 minutes) : S/N = 4300:1;

Table 2 Germanium detector S/N performances

Figure 3 Ge spectral response curve



Indium Gallium Arsenide detector (InGaAs).

-Operating temperature: room temperature;
-Detector size: 0.5 mm diameter;
-$D^*$ greater than or equal to 4.0x1012 cm Hz1/2 W-1;
-Useful spectral range: 5900 to 10000 $cm^{-1}$ (see figure 4);

Signal to Noise performances.
Tests performed:

1- Closed loop of 60 meters of ZrF Fiber (2x30 meters);
Fiber diameter = 250 microns;
Fiber N.A. = 0.2;
Preamplifier first stage feedback resistor = 1.8 MOhms;
Preamplifier gain = 1;
Spectral range = 7750 to 7850 $cm^{-1}$;
Resolution = 4 $cm^{-1}$;
Speed = 0.2 cm/sec optical;
The S/N ratio is an average of ten experiments and is a peak-to-peak value).

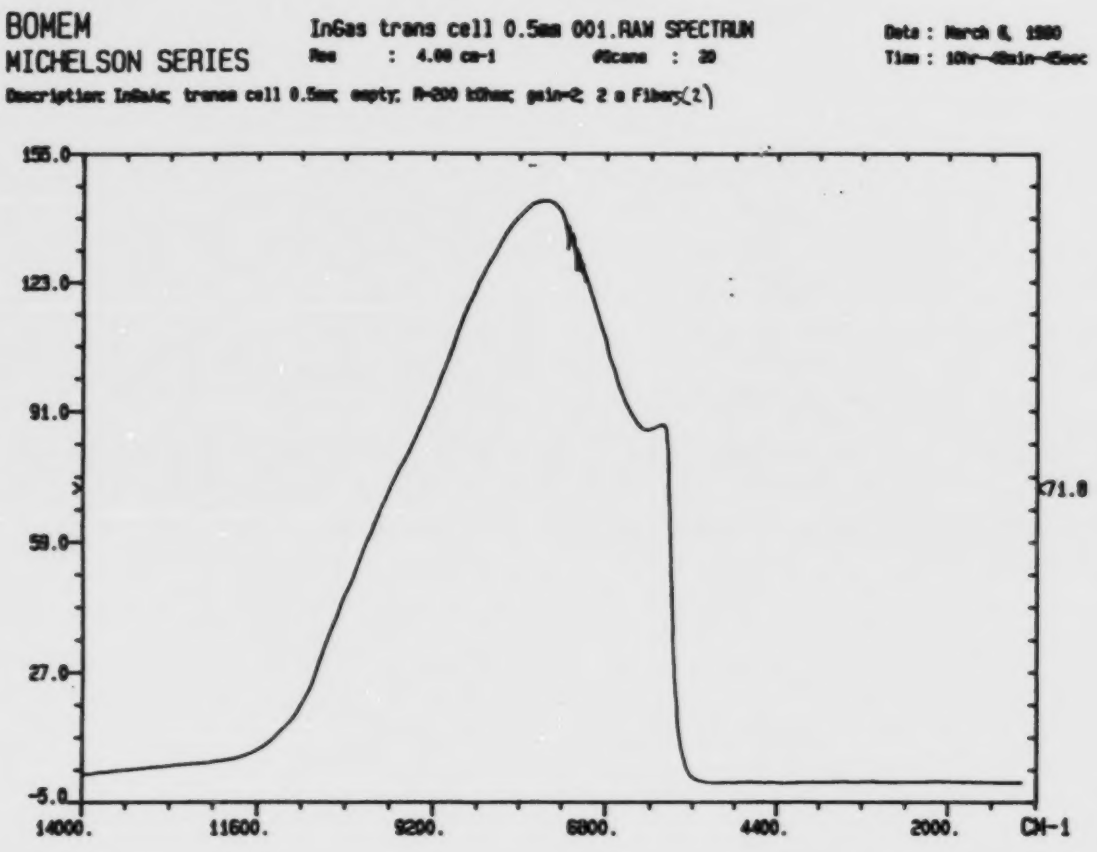
Results: 1 scan (≅7.5 seconds) : S/N = 578:1;
100 scans (≅2.5 minutes) : S/N = 2657:1;

2- 2x2 meters of ZrF Fiber + transmission cell;
Fiber diameter = 250 microns;
Fiber N.A. = 0.2;
Cell Windows: CaF2;
Window thickness: 3.6 mm (0.5 degree wedge);
Cell pathlength: 0.5 mm;
Cell was empty;
Preamplifier first stage feedback resistor = 200 KOhms;
Preamplifier gain = 1;
Spectral range = 7750 to 7850 $cm^{-1}$;
Resolution = 4 $cm^{-1}$;
Speed = 0.2 cm/sec optical;
The S/N ratio is an average of ten experiments and is a peak-to-peak value).

Results: 1 scan (≅1.5 seconds) : S/N = 825:1;
100 scans (≅2.5 minutes) : S/N = 3684:1;

Table 3 InGaAs detector S/N performances

Figure 4 InGaAs spectral response curve



Silicon detector (Si).

-Operating temperature: room temperature;

-Detector size: 1.1 mm x 1.1 mm;

-$D^*$ greater than or equal to 1.0x1014 cm Hz1/2 W-1;

-Useful spectral range: 10000 to 14000 $cm^{-1}$ (see figure 5);

-This detector should only be used in conjunction with the Corion filter provided with the system (model # LL-750)

Signal to Noise performances.

Tests performed:

1- Closed loop of 60 meters of ZrF Fiber (2x30 meters);
Fiber diameter = 250 microns;
Fiber N.A. = 0.2;
Preamplifier first stage feedback resistor = 5.0 MOhms;
Preamplifier gain = 4;
Spectral range = 10450 to 10550 $cm^{-1}$;
Resolution = 4 $cm^{-1}$;
Speed = 1.0 cm/sec optical;
The S/N ratio is an average of ten experiments and is a peak-to-peak value).

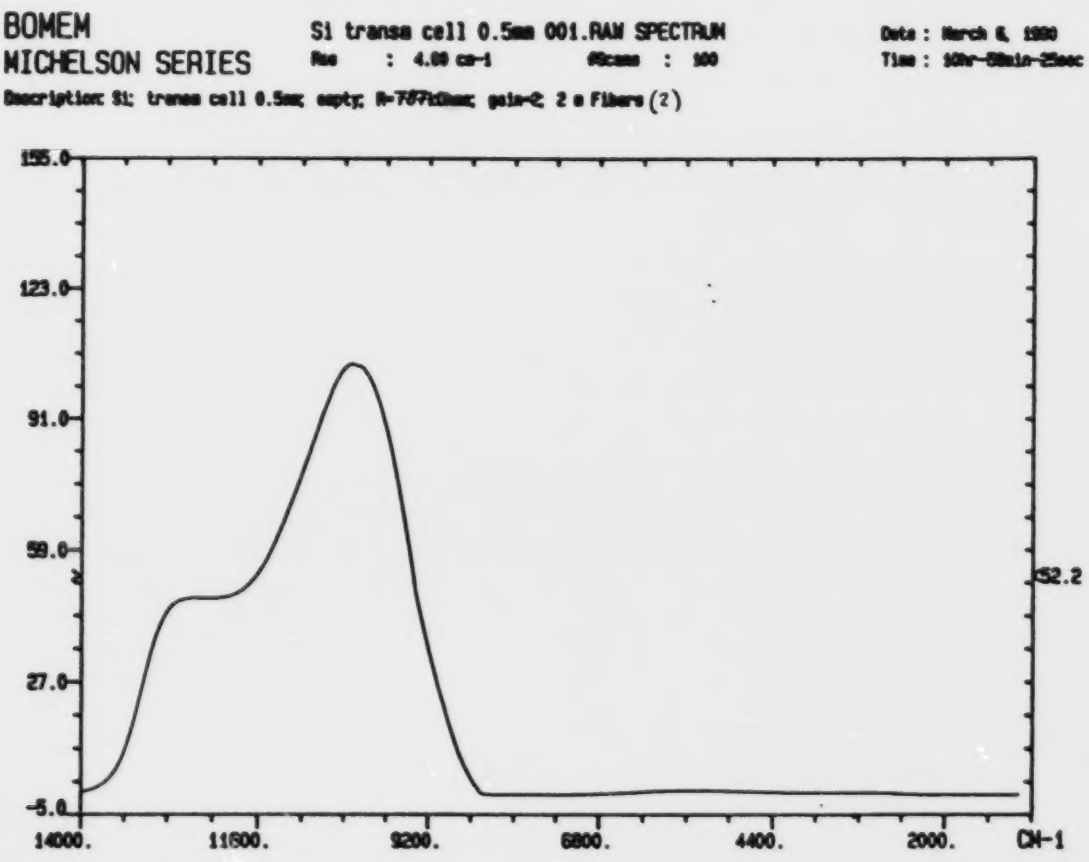
Results: 1 scan (≅ 1.5 seconds) : S/N = 35:1;
100 scans (≅2.5 minutes) : S/N = 329:1;

2- 2x2 meters of ZrF Fiber + transmission cell;
Fiber diameter = 250 microns;
Fiber N.A. = 0.2;
Cell Windows: CaF2;
Window thickness: 3.6 mm (0.5 degree wedge);
Cell pathlength: 0.5 mm;
Cell was empty;
Preamplifier first stage feedback resistor = 787 KOhms;
Preamplifier gain = 2;
Spectral range = 10250 to 10350 $cm^{-1}$;
Resolution = 4 $cm^{-1}$;
Speed = 1.0 cm/sec optical;
The S/N ratio is an average of ten experiments and is a peak-to-peak value).

Results: 1 scan (≅ 1.5 seconds) : S/N = 190:1;
100 scans (≅2.5 minutes) : S/N = 1852:1;

Table 4 Silicon detector S/N performances

Figure 5 Si spectral response curve



# 3. REMOTE SAMPLING

The instrument we designed for CANMET has a very special feature. Indeed, the sampling of the process is remotely performed, using fiber optics as a transmission medium for infrared radiation.

In this new design, we had to decide which fiber optics and which sampling strategy were to be used. Also, we had to design the fiber optics interface that would couple the interferometer output and detector input to the fiber optics themselves. The goal of this section is to talk about those topics.

## 3.1. Fiber Optics.

Using fiber optics in an industrial environment does have many advantages. One of those is the possibility of protecting the spectrometer by placing it in a safe environment, such as a control room. Fiber optics then allow the transmission of light from the spectrometer to the measuring points and back to the spectrometer. The small size and relative flexibility of the fibers make them particularly interesting for installation in very restricted spaces. Fiber optics are also extrinsically explosion proof and are well shock protected. There is also the possibility of time multiplexing several fiber optics circuits with only one spectrometer. Finally, fiber optics allow unprecedented freedom in choosing the sampling configuration allowing for geometries that were formally rarely encountered, and therefore opening new possibilities. Thus each sampling point could be independently optimized.

The choice of the fiber optics materials was based on the commercial availability of those and on the characteristics we were looking for. After carefully reviewing the fibers that were available, it was decided that Zirconium Fluoride (ZrF) fibers were to be used for the project, for the reasons listed below.

The transmission characteristics of the ZrF fibers were matching quite well the spectral range that had to be covered in the project. The statement of work for the project specified that the spectral range to be covered was from 1 to 4 microns (10000 to 2500 $cm^{-1}$), with a

possibility of going down to 0.7 microns (14300 $cm^{-1}$). The spectral transmission range of the ZrF fibers is from 0.3 microns up to 4.5 microns (33000 $cm^{-1}$ to 2200 $cm^{-1}$). The match was then suitable for this project.

Furthermore, the typical attenuation factor, associated to loss in the fibers, is typically from 20 to 100 dB/Kilometer (peak transmission), which were acceptable numbers for the project.

Also, those fibers were available in relatively large core diameter, and in lengths that were suited for the project. Finally, it was possible to get those fibers in a ruggedized cable, required for industrial applications.

The fibers that were finally chosen came from Iris Fiber Optics, inc. Those have a core diameter of 250 microns (the largest diameter available at that time), with a clad diameter of 330 microns. The Numerical Aperture (N.A.) of those ZrF fibers is 0.21. The refractive index is $\cong 1.5$ (see Appendix E for the Iris product information).

Two (2) pairs of ZrF fibers were provided. The length of the first pair of fibers was 30 meters, and those fibers were intended for remote applications into a real industrial environment. The length of the second pair of fibers was 2 meters, and those were intended for a laboratory environment.

Those two (2) pairs of fibers were provided as industrial grade cables, i.e. they were constructed using a lined stainless steel braid that was fitted with SMA 905 type end connectors.

Also, very early in this project, we have ordered, from Guided Wave, inc., two (2) Quartz (Silica) fiber optics. The length of those fibers is 2 meters. The core diameter is 500 microns. Those fibers have a PVC coated Aluminum monocoil jacket terminated with SMA type end connectors. The spectral transmission range of the fibers is from 0.4 micron up to 2.1 microns (25000 $cm^{-1}$ down to 4750 $cm^{-1}$). Those fibers were ordered along with the Wang (dip type) probe, to be used with it.

## 3.2. Sampling strategy.

For this project, we have retained the following sampling strategy (see figure 6).

So-In-FO1-SH-FO2-De

where "So" is the infra-red source;
"In" is the interferometer;
"FO1" is the fiber optics cable bringing the infra-red energy from the spectrometer to the Sampling Head;
"SH" is the Sampling Head;
"FO2" is the fiber optics cable bringing the infra-red energy from the Sampling Head back to the spectrometer;
"De" is the infra-red detector.

This configuration is called the "normal" configuration in which the "FO1-SH-FO2" arrangement replaces the more usual sampling accessory. Note also that in this configuration, the detector is positioned close to the interferometer, and is in fact part of the whole spectrometer.

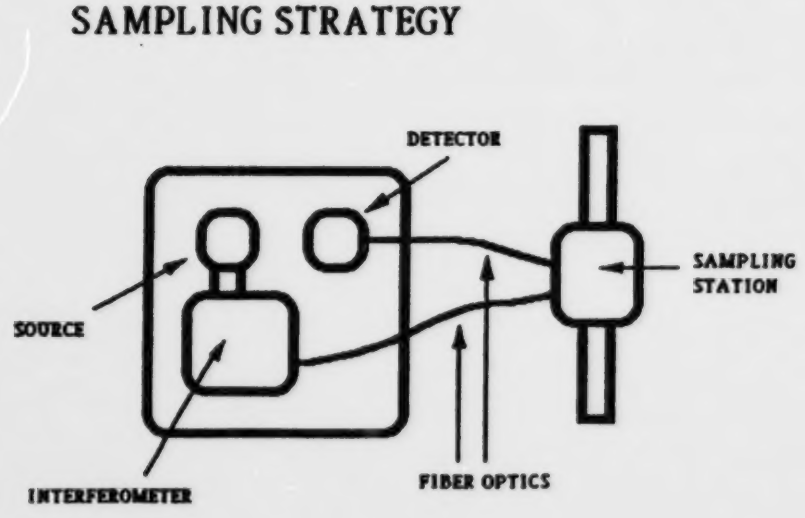



Figure 6 Sampling strategy (normal configuration)

## 3.3. Fiber Optics Interface.

The fiber optics interface we designed had to couple the modulated infra-red energy coming from the interferometer to the round entrance of the fiber end.

Our design criteria were based on some characteristics of the fiber, mainly the diameter of its core and its Numerical Aperture.

One of the main limitation using fiber optics comes from the relatively low geometrical coupling efficiency (low throughput of the fiber). This throughput or "étendue" ($\theta_{fiber}$) is defined as being the product of the area of the core of the fiber optics ($Area_{fiber}$) and of the solid angle of collection of the fiber ($\Omega_{fiber}$). See figure 7

$$\theta_{fiber} = Area_{fiber} * \Omega_{fiber}$$

where $Area_{fiber}$ is expressed in $cm^2$
and $\Omega_{fiber}$ is expressed in steradian.

In order to maximize this throughput, the fibers with the largest core diameter commercially available were ordered, i.e. 250 microns. The Numerical Aperture is a characteristic of the materials used in the fabrication of the fibers, and is being defined as:

$$\sqrt{n_1^2 - n_2^2}$$

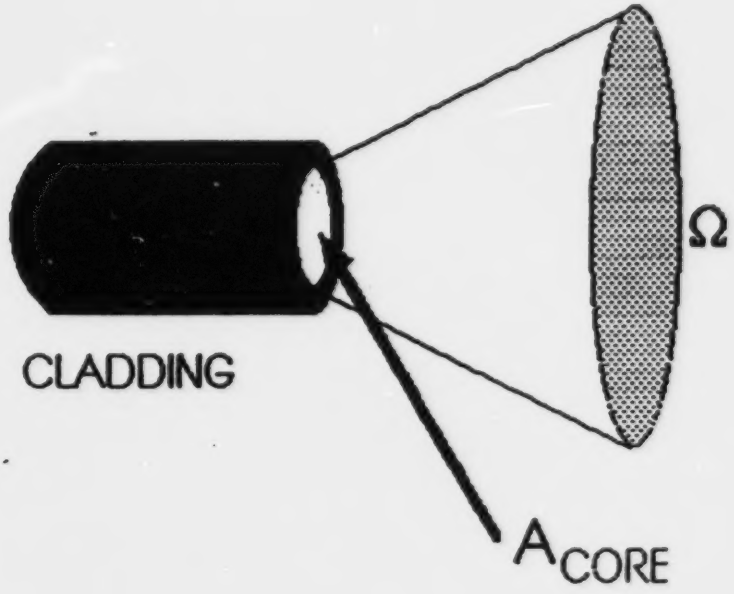
where $n_1$ is the refractive index of the fiber core;
and $n_2$ is the refractive index of the fiber clad;
(where $n_2 < n_1$).

The fibers we have ordered had a Numerical Aperture of 0.21 (which is a nominal value for a glass clad Zirconium Fluoride fiber).

Figure 7 Fiber optics coupling

# FIBER OPTICS COUPLING

## Low Geometrical Coupling Efficiency




Throughput of NIR-FTIR : $A\Omega = .0011\ cm^2sr$
Throughput of Fiber : $A\Omega = .00007\ cm^2sr$
for 250μm and NA = .21

Based on those previous values, the geometrical throughput of the fiber ($\theta_{fiber}$) is then:

$$Area_{fiber} = \Pi/4 * (0.025)^2 = 0.000491 \text{ cm}^2$$

$$\theta_{fiber} = 2\Pi \{1-\cos[\sin^{-1}(N.A.)]\}$$

$$= 2\Pi \{1-\cos[\sin^{-1}(0.21)]\}$$

$$= 0.140 \text{ steradian.}$$

$$\text{Then } \theta_{fiber} = 0.000491 * 0.140 = 0.000069 \text{ cm}^2 \text{ sterad}$$

$$\theta_{fiber} \cong 0.00007 \text{ cm}^2 \text{ sterad}$$

It is then interesting to compare this geometrical throughput to the throughput we would have when not using a fiber optics interface (this new value will be defined here as being the full throughput value, ($\theta_{full}$). The computed value for this throughput is based on some interferometer and infra-red source characteristics, and is equal to:

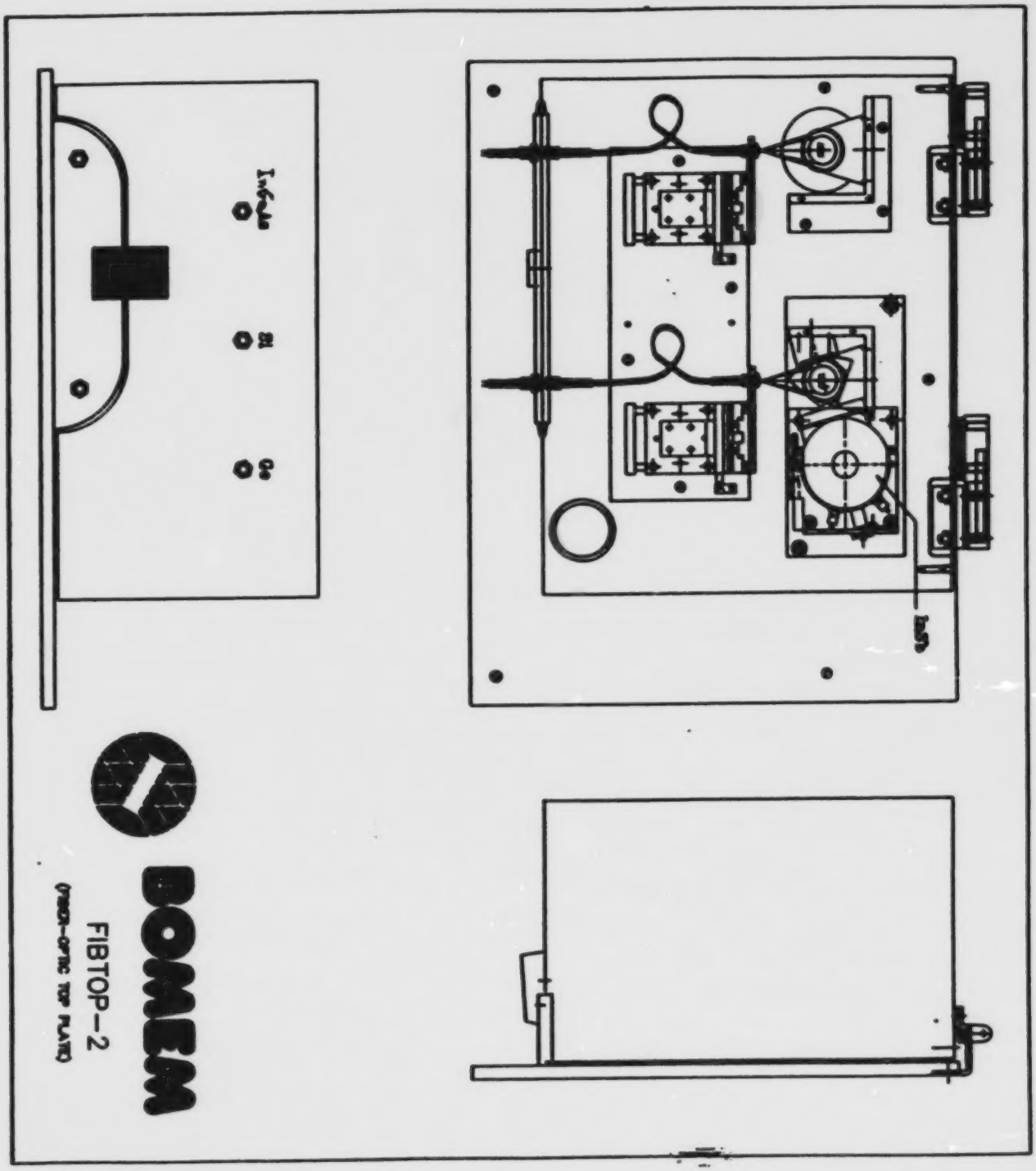
$$\theta_{full} = 0.0011 \text{ cm}^2 \text{ sterad}$$

The ratio between the fiber throughput ($\theta_{fiber}$) and this full throughput ($\theta_{full}$) is then equal to:

$$\frac{\theta_{fiber}}{\theta_{full}} = \frac{0.00007}{0.0011} = 0.0636 \cong \frac{1}{16}$$

which means that, when using the fiber optics interface, we are actually using only 1/16 of the available infra-red energy (the transmission level is then around 6%). Although this transmission level appears to be small, it is nevertheless sufficient for performing the foreseen applications (the fiber optics interface is schematically represented on figure 8).

Figure 8 The fiber optics interface



Our major concern in designing this accessory was to provide to the fiber input a beam that would fill entirely both the fiber core area and the fiber Numerical Aperture.

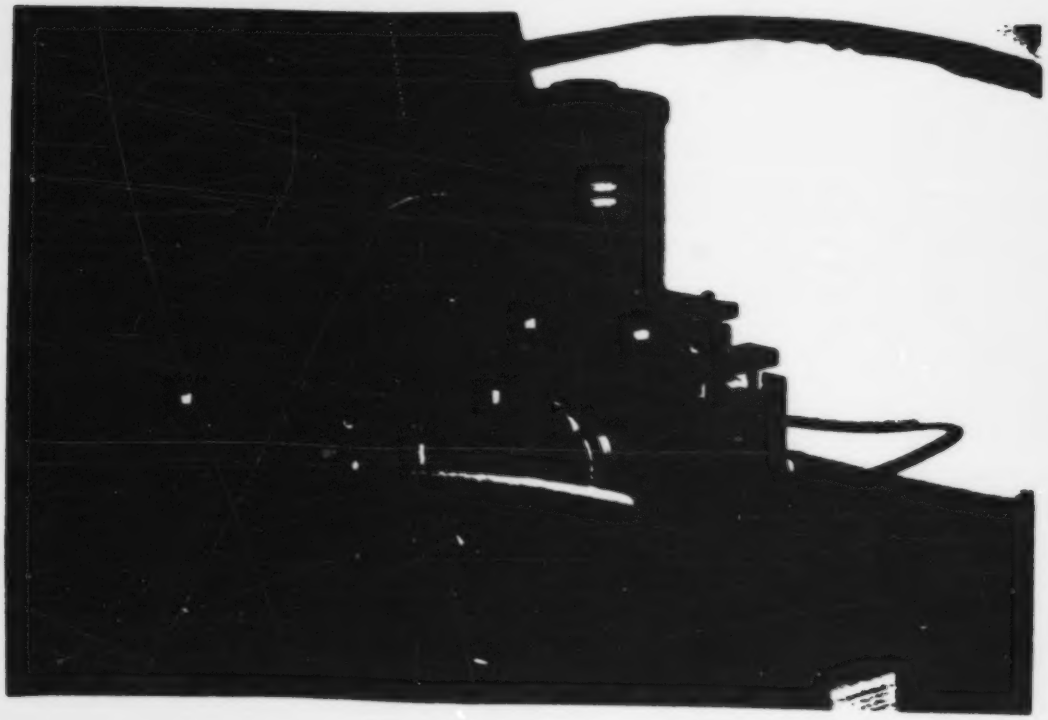
The modulated infra-red beam coming out of the interferometer portion is a 1 inch diameter circular collimated beam. To focus that beam on the fiber end, we had to use a parabolic mirror. The focal length of this mirror has been chosen to be 1.75 inches. Using this mirror, the focal spot falling on the fiber end has now a diameter of $\cong$ 500 microns, and a converging half-angle of $\cong$ 17 degrees, which translates, in term of Numerical Aperture, to a value of 0.3. Both the spot diameter and the beam N.A. are larger than the fiber diameter and the fiber N.A., which means that our fiber optics interface is correctly matching the throughput allowed by the fiber characteristics.

The fiber on which the infra-red energy coming from the interferometer falls on is called the output fiber. Its end connector is mounted on a XYZ positioner, which gives the possibility of adjusting the fiber end in front of the focal spot, in order to maximize the energy going into the fiber core.

We knew that, using our FT-NIR spectrometer, the users would swap often from one pair of fibers to the other. In order for them not to care about aligning the fibers ends each time there was a change, we have decided to provide the fiber optics interface with an intermediate Zirconium Fluoride fiber. One end of this fiber is mounted on the XYZ positioner, enabling the positioning of it in front of the incoming infra-red beam. The other end is mounted on a bulkhead feed through, enabling the proper connection of two fiber ends, both terminated with SMA 905 connectors. By doing so, it was also possible to cover the entire optical components, giving now the possibility of purging this enclosed space (usually with nitrogen gas). The user has just now to screw the fiber connector on the feed through, without caring for the fiber alignment.

To couple the radiation back to the InSb detector, we have been using the same process,i.e. a bulkhead feed through, then an intermediate ZrF fiber mounted on a XYZ positioner in front of a parabolic mirror, 1.75 inches focal length. The collimated beam is then sent on a second parabolic mirror, this time with a 0.875 inches focal length. This mirror then focuses the radiation on the InSb detector.

For the Germanium, Indium Gallium Arsenide and Silicon detectors, the coupling process is much simpler. Indeed, those detectors are mounted into a special receptacle, designed to be used with fiber optics having SMA end connectors. By screwing the fiber optics on to this receptacle, the fiber end is in contact with the detector window. The beam is simply diverging, falling then on the detector surface. It requires no optical component between the fiber end and the detector, and by the way no optical alignment is required.



Picture 2 Fiber optics interface with InSb detector

# 4. ACCESSORIES

The accessories represent the interface between the process (i.e. the sample to be analyzed) and the measuring equipment (i.e. the spectrometer). The accessory that is to be used in a defined process depends mostly on the type of sample to be analyzed (gaz, liquid, solid, emulsions, etc.). Different sampling techniques are thus required when sampling different types of sample. Also, using more than one sampling technique for the same sample may prove to be useful for getting more information on it. The goal of this section is thus to present the accessories that were provided with the system, keeping in mind that all those had to be provided with a fiber optics coupling.

## 4.1. The Transmission Cell Accessory.

A common method to obtain infrared spectra of liquid samples is to use a transmission cell. The normal arrangement is to seal a sample between two salt windows and collect the IR radiation that is transmitted through the sample and windows to obtain the IR transmittance spectra for the sample, when the ratio to a reference spectra is made. A transmission cell, from Harrick Scientific Corp., has been used which allows for a flow of liquid through the cell. Since liquids are known to absorb strongly in the infrared region, various spacers are used between the CaF2 windows to control the pathlength in the cell. The limitations of the required pathlength has been shown to be a source of problems encountered in using the cell. These problems have been discussed extensively in previous reports.

The system used is unique to previous ones using a transmission cell. A fiber optics coupled interferometer is used to pass the infrared radiation to and from the sampling area. In the sampling area, the radiation originally from the interferometer is optically collimated to travel through the transmission cell, then refocussed back to an exiting fiber which carries the radiation to a detector (see figure 9). Throughput limitations of the fiber, which have been a problem for use with other types of sampling accessories, have not affected the performance of the cell when using thin spacers. Useful and reproducible results have been obtained for analysis in our tests at Bomem.

However these preliminary tests experienced problems which resulted in the breakage of the CaF2 windows. It is assumed that the presence of weaknesses in the windows due to scratches or chips, and the lack of experience with the flow of viscous liquids are to blame for these problems. The utmost care must be taken in handling of the fragile and brittle windows, while the flow of the sample must be scrutinized. The $CaF_2$ windows supplied are not of constant thickness, but are wedged with a .5 degree angle. The wedged windows are used to reduce any interference effects that may occur. The high end has been marked on each window.

The flow of the liquid sample is accomplished by use of a pump and tubing with appropriate connectors. To aid in the flow of viscous samples, the cell is equipped with a heating jacket and temperature controller. The cell can withstand pressures up to 100 PSI, and temperatures up to 100 degrees Celsius.

The transmission cell has shown to give results that are quite useful to the spectral analysis of liquid samples. The analysis of the obtained spectra, either qualitative or quantitative, is dependent on the decision of what thickness of spacers to be used along with spectral areas of interest.

Picture 3 Transmission cell accessory

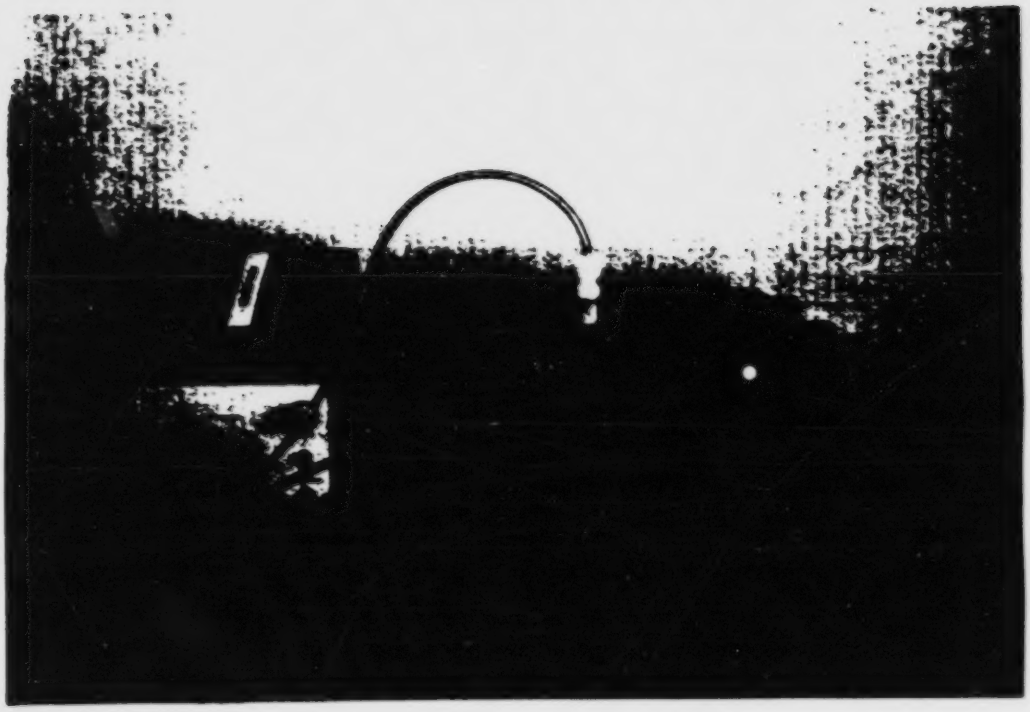
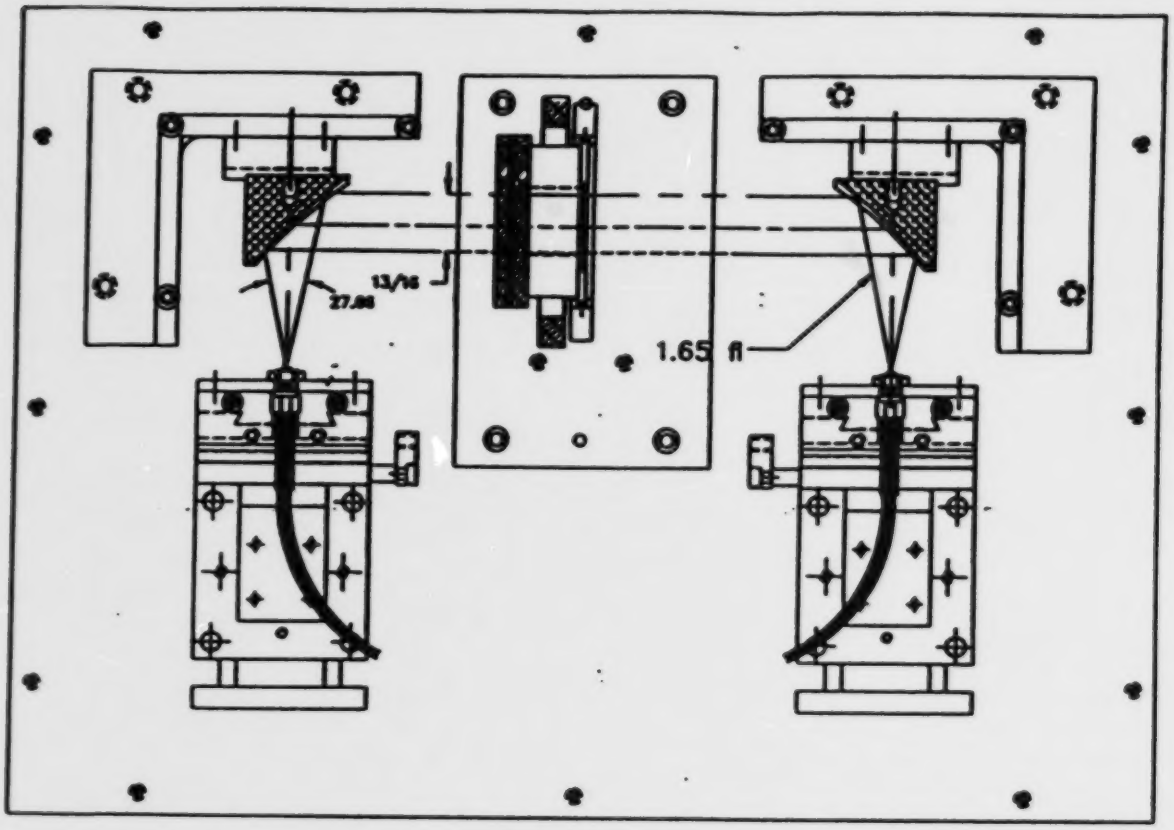


Figure 9 Transmission cell schematic



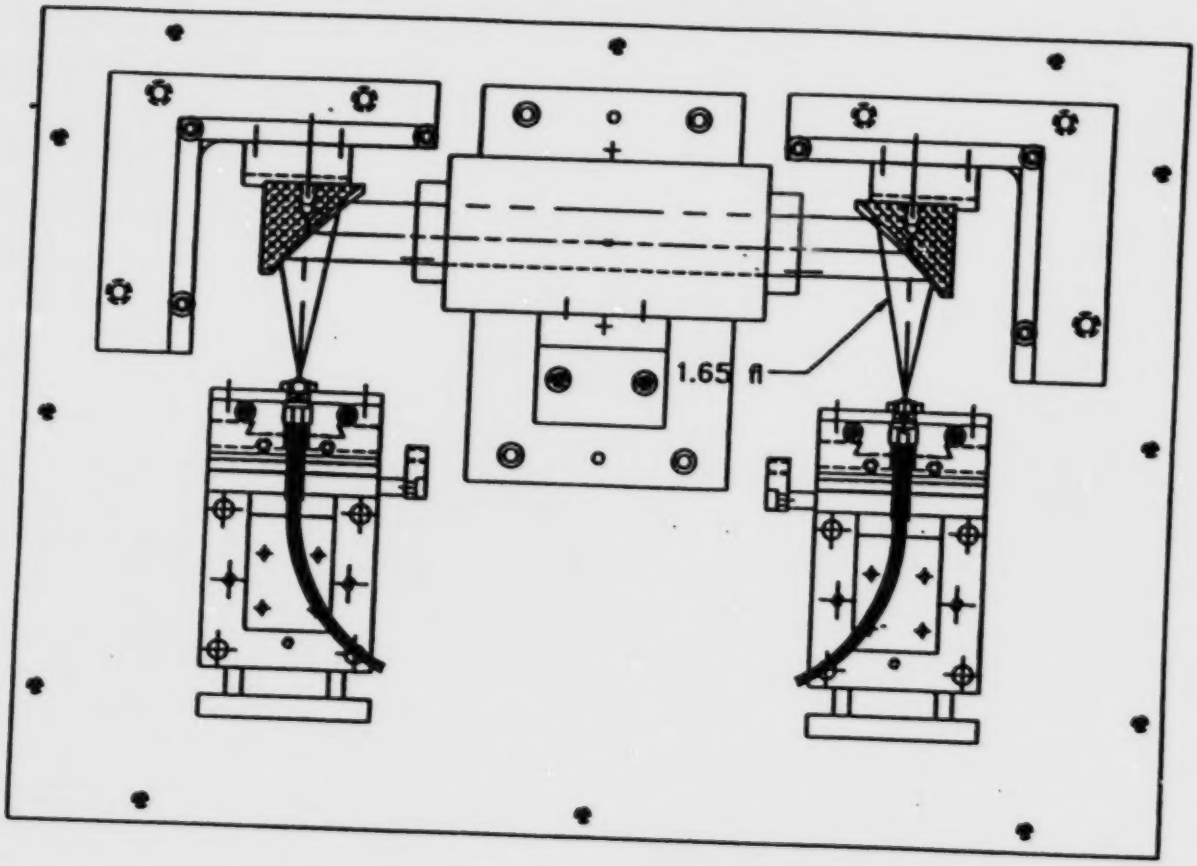
## 4.2. The ATR Accessory (Tunnel Cell).

Internal reflectance spectroscopy is a method used for infrared spectral analysis of liquids or solids. The optical properties of the method have allowed the analysis of highly absorbant liquids (such as water) to be easily made. There are various types of attenuated total reflectance (ATR) accessories that are available on the market, such as; the Circle Cell by Spectra Tech and the Tunnel Cell by Axiom Analytical, which are most familiar to most in the field. For the application of on-line analysis of oil-water emulsions, the Tunnel Cell has been chosen for its ruggedness making it suitable in an industrial environment. The principles and practical application of the cell have been investigated at Bomem, recently. These tests have shown that there are specific concerns in using the Tunnel Cell that must be addressed.

The Tunnel cell is an ATR accessory produced by Axiom Analytical Inc., located in California (see Appendix F for the product description). The basis of the cell is quite simple and intuitively basic, however, the electromagnetic considerations (the `guts' of the cell) are what enable the cell as an analytical tool.

The cell basically consists of a ZnSe crystal, which is cylindrical in shape with conical ends, mounted in a stainless steel cavity by use of O'rings at each end of the cell. The central part of the incident beam of radiation, that would directly reach the crystal face, is blocked, while the outer portion of the incident radiation to the cell is reflected by an end cone, surrounding the conical end of the crystal. This ensures that all radiation will enter the crystal perpendicular to the conical end to reduce any reflection or refraction at the surface of the crystal interface. This radiation will pass through the crystal and undergo total internal reflection due to the incident angle (45 degrees determined by entrance configuration) exceeding the critical angle of the crystal. The reflected angle and the length of the crystal predetermines that all beams of radiation will undergo the same number of reflections (which is important to maintain a constant effective path length) and will exit the opposite end of the cell in the same manner that it entered (see figure 10).

Figure 10 ATR accessory schematic



The cell used is the Tunnel Cell model #TNL-131C which is equipped to handle a flow of liquid sample pass the crystal. Included with the cell are: two external ports that allow the passage of liquid to and from the cell, helical threading within the cell to provide mixing and a heating cartridge with thermocouple to aide in the flow of viscous material. These features combine to present a rugged and useful accessory.

Electromagnetic theory can be used to show that the radiation through the cell is totally reflected, but, there occurs an interaction at the surface of the crystal with the sample. In the crystal, or internal reflectance element (IRE), a standing wave, or evanescent wave, is established near the surface of the crystal where the amplitude of the electric field of the radiation decreases exponentially with distance away from the surface of the IRE. The distance at which the electric field reaches 1/e of its initial magnitude is defined as its penetration depth ($d_p$), which is dependent upon wavelength of radiation (l), refractive index of the crystal ($n_p$), refractive index of the sample ($n_s$), and the angle of incidence at the surface of the IRE (A), and this can be given by:

$$d_p = \frac{l}{Pi\ n_p\ [\sin^2 A - (n_s/n_p)^2]^{1/2}}$$

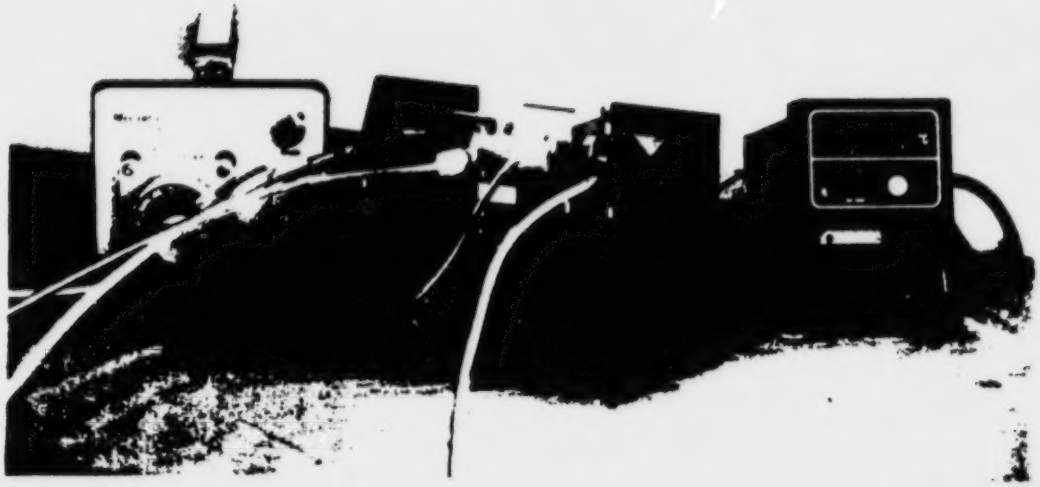
The interaction of evanescent wave and the sample gives the resulting absorption spectra. It should be noted that in the region of an absorption band, the refractive index of the sample will change dramatically, changing the depth of penetration.

Some of the implications of this theory must be kept in mind during the analysis of obtained spectra. From the equation for the depth of penetration, the dependency of wavelength and refractive index of the sample must be considered. The wavelength region that we will mainly deal with (near infrared region) will typically yield depths of penetration below one micrometer, thus only the sample in direct contact with the IRE will interact with the emanating evanescent wave. Also, the variation of $d_p$ with wavelength will cause distortions of band absorbances so that ATR spectra will not compare favorably to transmission spectra, which is more commonly seen in library spectra. Distortion of band shape can occur, as well, due to the dependency of the sample's refractive index, for in the vicinity of absorption bands the varying $n_s$ will cause changes in $d_p$. Since the field of ATR spectroscopy is relatively new, these aspects must be carefully scrutinized when using the technique and direct comparison of spectra obtained by other methods may not always be self-evident.

Problems were encountered while using the Tunnel Cell. Two main concerns were: the low transmission of the cell resulting in poor signal to noise ratios, and the residual effects shown in the obtained spectra.

The low transmission values for the cell is due to low throughput using the fibers. The main reason is that the exiting beam from the cell has more divergence than first expected, which decreases significantly the collection efficiency of radiation to the fiber resulting in lower detection. In order to increase the throughput would require a larger area for the input beam, which can only be achieved by using a fiber bundle. This has been a fact that is becoming more apparent for this type of system-accessory configuration, seen in this and other studies with the fiber coupled interferometer. A fiber optic bundle would allow for flexibility in remote measurements and would be an advantage to increase the throughput limitations, however, the fiber optic bundles are expensive and may not be economically feasible for most uses.

The spectra obtained for the samples in our study have shown a definite appearance of residual effects. Some of the residuals were found to be due to material collecting within the cell and not being expelled using solvents. A better method to flush the cell will have to be discussed to ensure that this does not happen continuously. There were also effects seen due to an affinity of water to the ZnSe crystal which appeared often throughout the study. Water, a highly polar molecule, collecting on the crystal can form a layer which will interfere with other features. Using the equation for depth of penetration ($d_p$), approximate depths can be calculated for various wavelengths as shown in table 5.



Picture 4 ATR accessory (Tunnel Cell)

**ZnSe crystal:**

$n_p = 2.4$

$n_s = 1.3$ (water)

incident angle = 45 °

critical angle = 32.8 °

| Wavelength | | Depth of Penetration |
|---|---|---|
| $cm^{-1}$ | microns | microns |
| 2000 | 5.00 | 0.73 |
| 3000 | 3.33 | 0.49 |
| 4000 | 2.50 | 0.37 |
| 5000 | 2.00 | 0.29 |
| 6000 | 1.67 | 0.24 |
| 7000 | 1.43 | 0.21 |
| 8000 | 1.25 | 0.18 |
| 9000 | 1.11 | 0.16 |
| 10000 | 1.00 | 0.15 |

Table 5 Depth of penetration of radiation

From these calculations it is apparent that even a very thin layer (less than one micrometer) of water on the crystal could impair the measurements taken. The spectra that have been observed have shown the influence of residuals in the cell, which has severely limited the ability of the cell as an analytical tool.

## 4.3. Cladless Sapphire fiber used as an ATR.

An appealing way of performing ATR spectroscopy is by using a fiber optics as the sampling medium. Indeed, a fiber stripped of its external cladding, which is called a cladless fiber (only the core of the fiber is present), becomes an ATR. By embedding this cladless fiber into a fluid of interest (the sample), one could then perform ATR spectroscopy. By doing so, the coupling efficiency of the two (2) fiber optics used as a transmission medium (light guide) and the fiber used as an ATR is relatively high (usually more than 20%). However, because of the relatively small area of interaction between the fiber and the sample, the sensitivity of this sensor might not be as good as a standard ATR rod.

Starting from those considerations, the idea was then to design an accessory based on this appealing approach. Lacking expertise for designing such an accessory, BOMEM then had to rely upon the expertise of IRIS Fiber Optics, inc. (our Zirconium Fluoride fibers supplier). IRIS has gained expertise by designing, manufacturing and using that technology. We have gave them the task of packaging a cladless fiber into a one inch pipe, providing them with all the information available on the samples and on the flow characteristics found inside the experimental mini-plant in Devon, Alberta.

As for the fiber material itself, it was decided to go with a cladless Sapphire ($Al_2O_3$) fiber. Sapphire posses a unique combination of physical, mechanical, and chemical properties that makes it a very good candidate for this application. Because of its extreme surface hardness, Sapphire can be scratched by few substances other than itself. Since it is chemically inert and insoluble in most solutions, it can be easily cleaned using various solvents. Also, because of its high melting temperature (2000 $^{\circ}C$) and high thermal conductivity, Sapphire can be effectively heated without risk of breaking the fiber. Because of its strength, Sapphire fibers should be able to withstand pressure and strain under a flowing liquid situation. Furthermore, in order for the ATR technique to give results, it must be understood that the ATR medium refractive index must be larger than the sample fluid refractive index. The refractive index for the Sapphire is $\cong 1.7$, which is a good figure for fluids having a refractive index of $\cong 1.5$ or less (which is the case for the majority of oil/water emulsions).

The ATR sensor final design is presented on figures 11 and 12. The general specifications of this accessory are also presented in Table 6. As mentioned earlier, it has been designed to be installed in the oil mini-plant in Devon, Alberta. The way it will be installed in shown on figure 13.

The EWS 1-6 sensor is designed for obtaining on-line infrared spectra of a process stream. Since the sensor fiber sensitivity falls off rapidly with distance from the surface of the sapphire fiber, the sensor is most useful with streams which will not selectively deposit a helm on the fiber.

General Specifications:

| | |
|---|---|
| Wetted materials: | 316 stainless, Teflon, Buna N |
| Design pressure: | 150 psi |
| Proof pressure: | 600 psi (static charge) |
| Operating temperature: | 0ø - 100ø Celsius |
| Pipe connections: | 1" NPT, male in line, 10" apart |
| Weight: | 6 lbs. |
| Fiber cable connection: | accepts either standard SMA 905 or IRIS Process Hard connector. |
| Sensor element:<br>Diameter<br>Active length | Optical sapphire fiber<br>.010 in (250 microns)<br>6.0 inches |
| Usable spectral range: | 2500 - 8000 $cm^{-1}$ |

Table 6 Specifications of the Evanescent Wave Probe

Figure 11 Evanescent wave sensor (ATR)

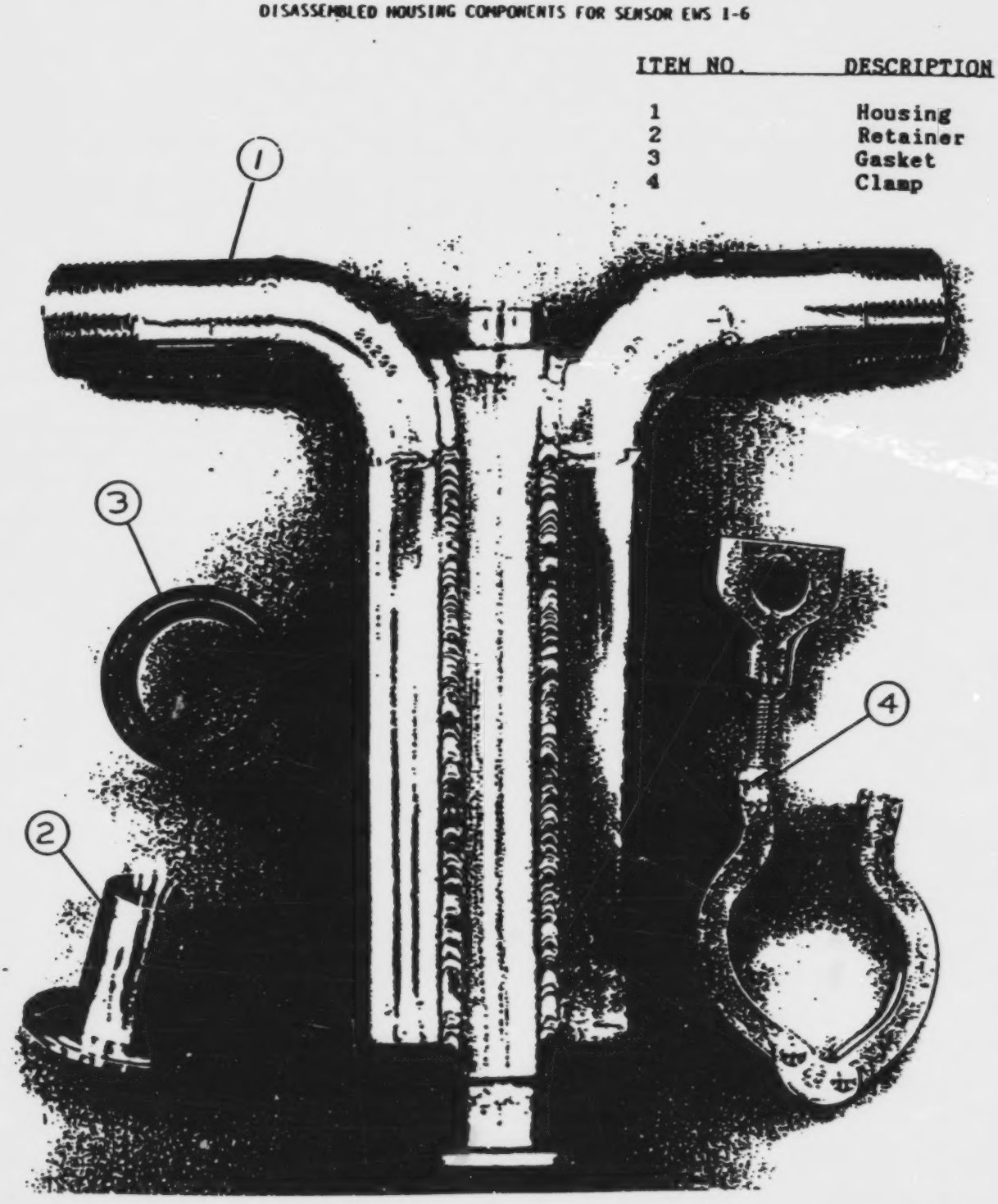
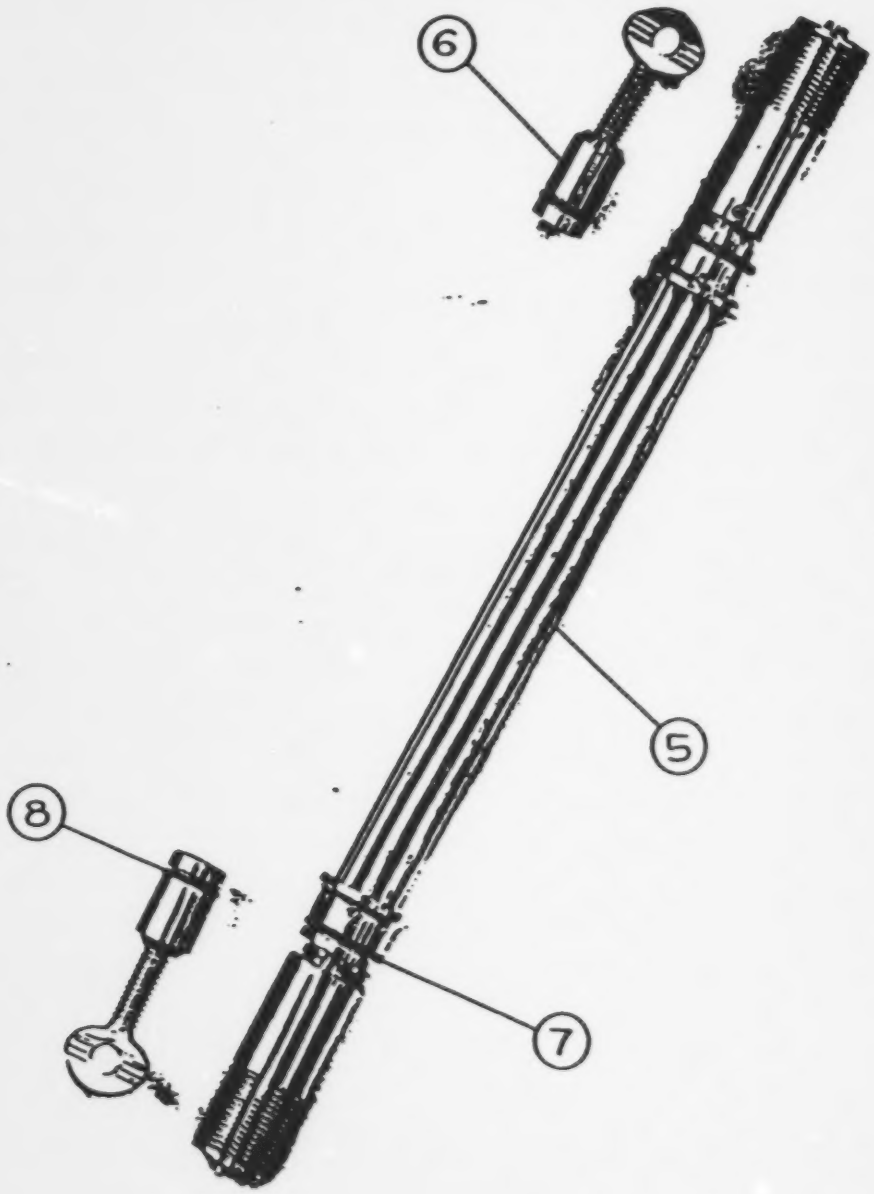


Figure 12 Sensor element (cladless sapphire fiber)

SENSOR ELEMENT AND PROTECTIVE END CAPS

| ITEM NO. | DESCRIPTION |
|---|---|
| 5 | E.W. Sensor Element (6") |
| 6 | Protective Cap |
| 7 | O-ring (2-016) |
| 8 | O-ring (2-012) |



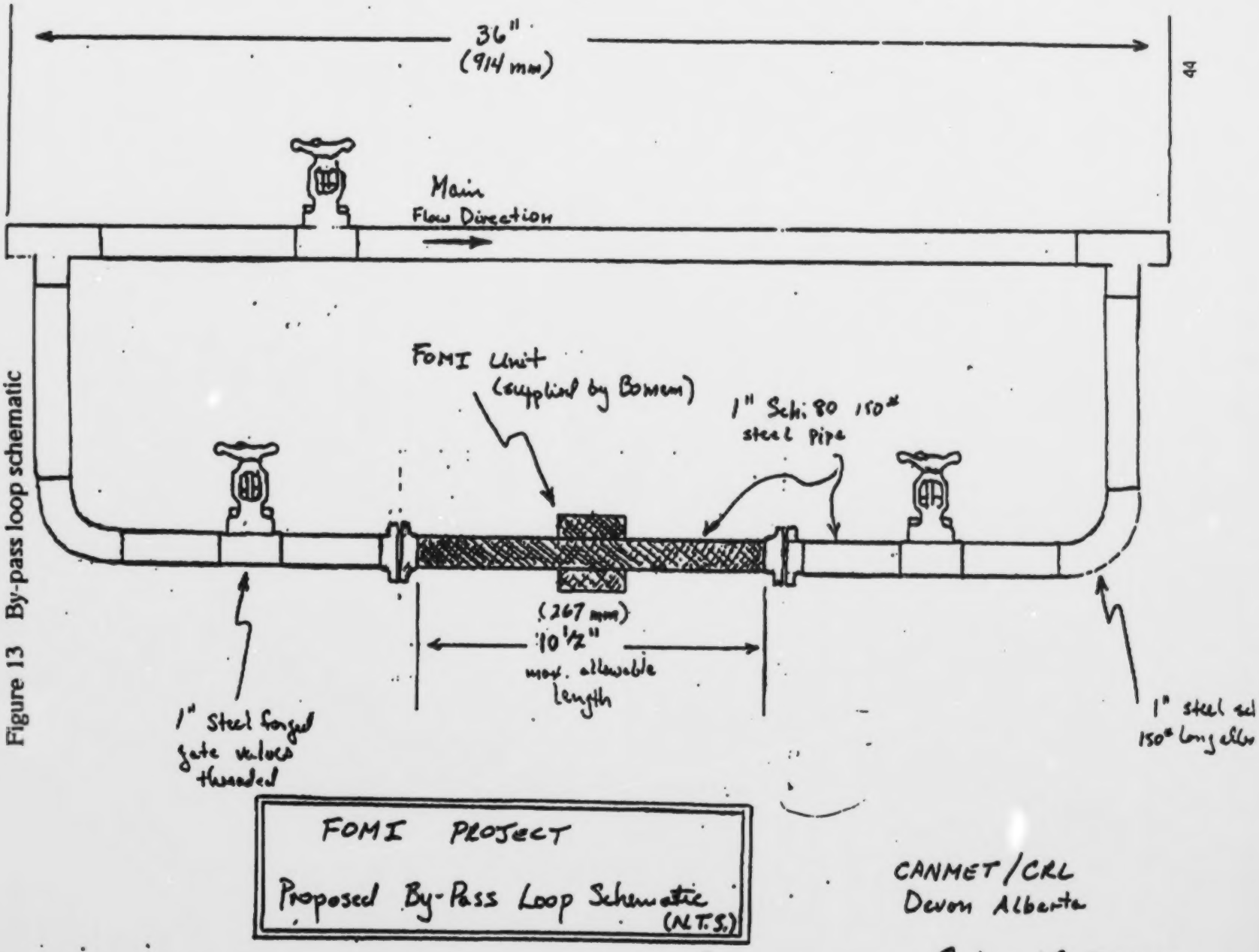
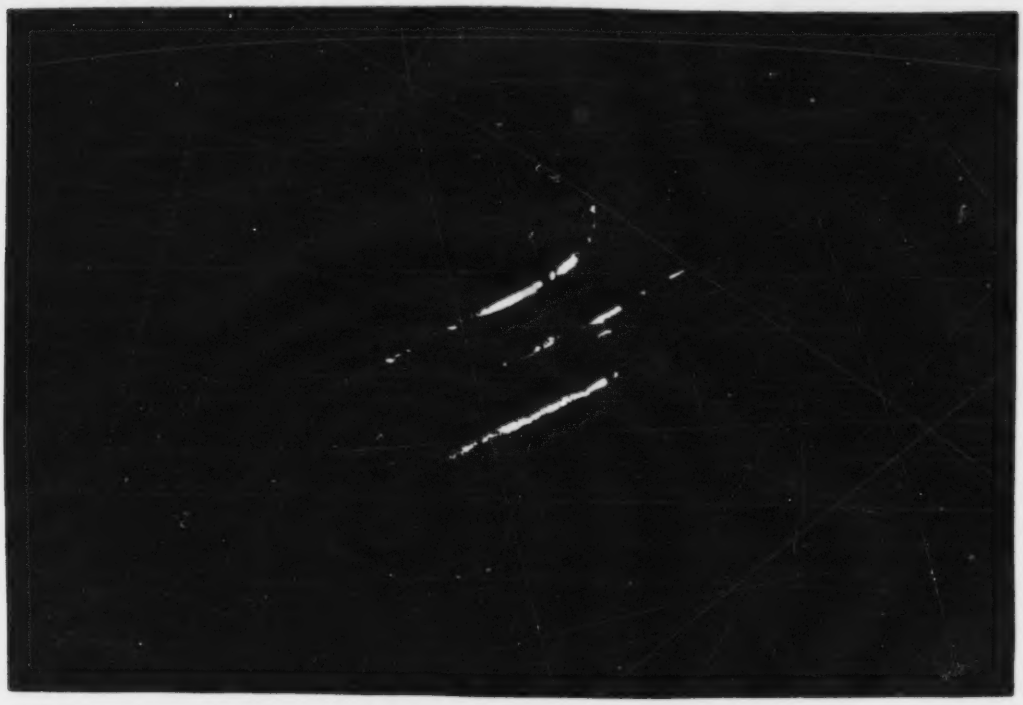
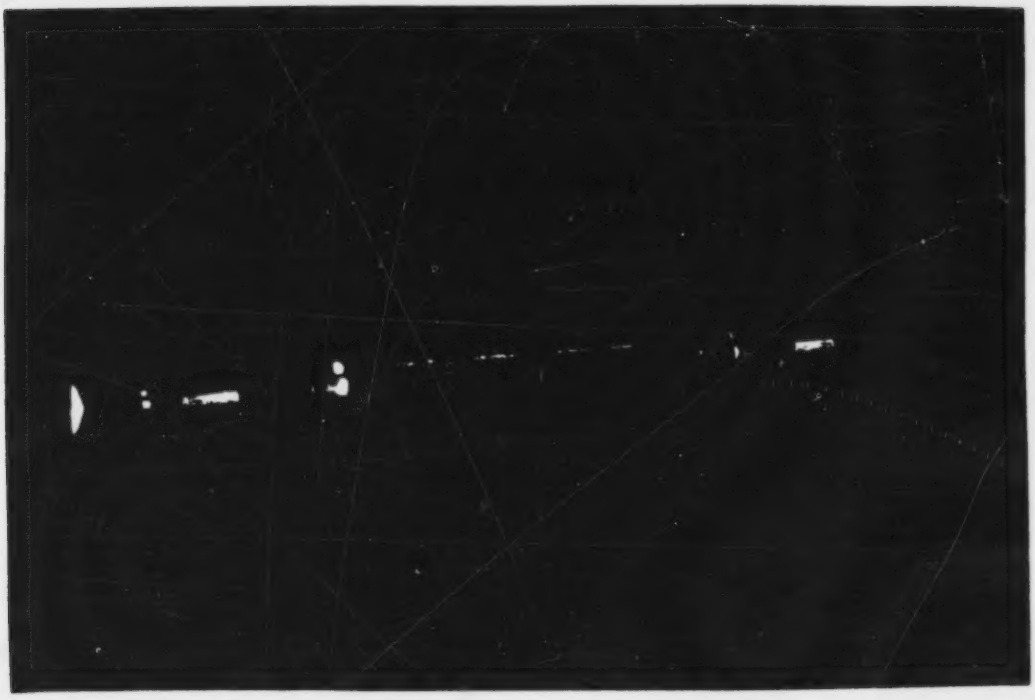



Figure 13 By-pass loop schematic

Picture 5 Evanescent wave sensor



Picture 6 Sensor Element (cladless sapphire fiber)



During the installation process back in Devon, we have been able to perform some tests using this ATR accessory. One of those consisted in looking at oil spectra, mixed with different quantity of water (i.e. oil/water emulsions). This emulsion was then flowed through the accessory. We have performed this test using the InSb detector only. We have performed it with different oil/water concentrations, which were:

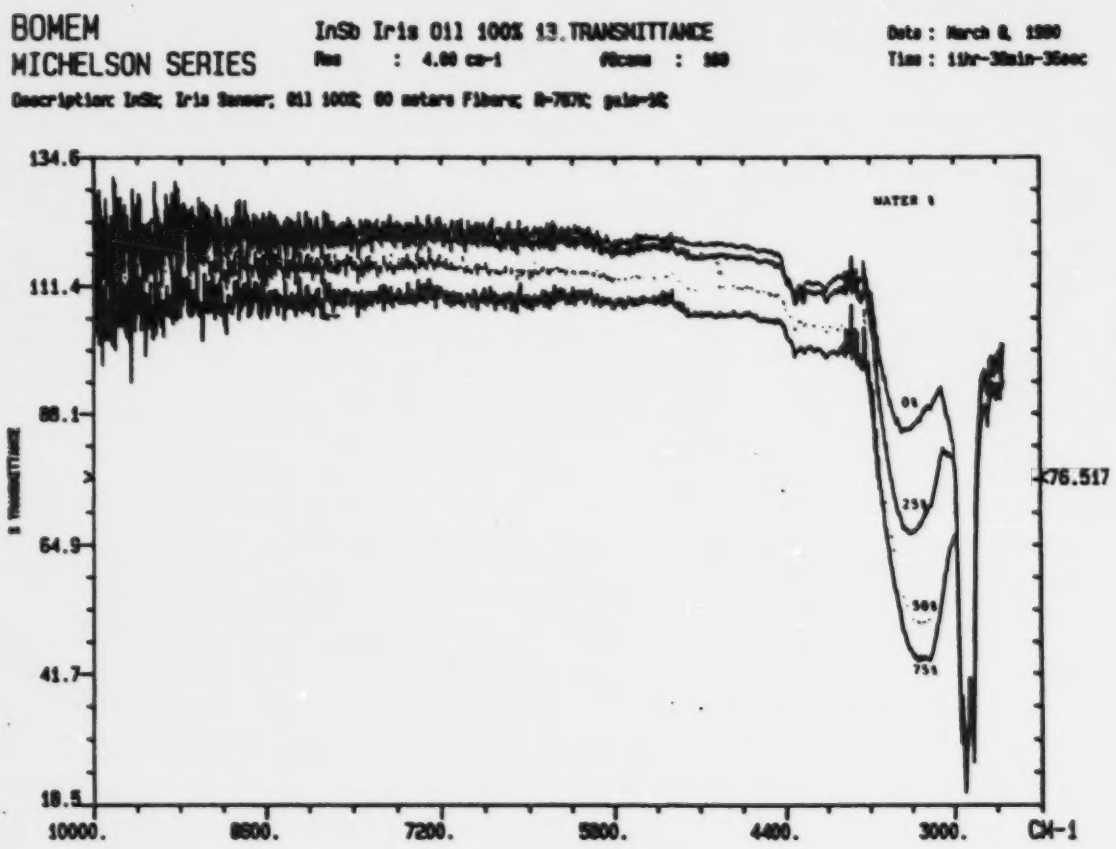
oil, 0% water;
oil, 25% water;
oil, 50% water;
oil, 75% water;

(those values are all computed on a volume basis).

Figure 14 shows the different results we have obtained (all the spectra are showed on the same scales). It seems that by adding water to the oil, the oil bands do not change, but that the water band (at 3400 $cm^{-1}$) increased with increasing amount of water.

Looking at the results we have obtained from those tests and from a few other ones, we can conclude that this accessory has performed well, even though a lack of sensitivity has been noted when trying to perform spectroscopy in the NIR.

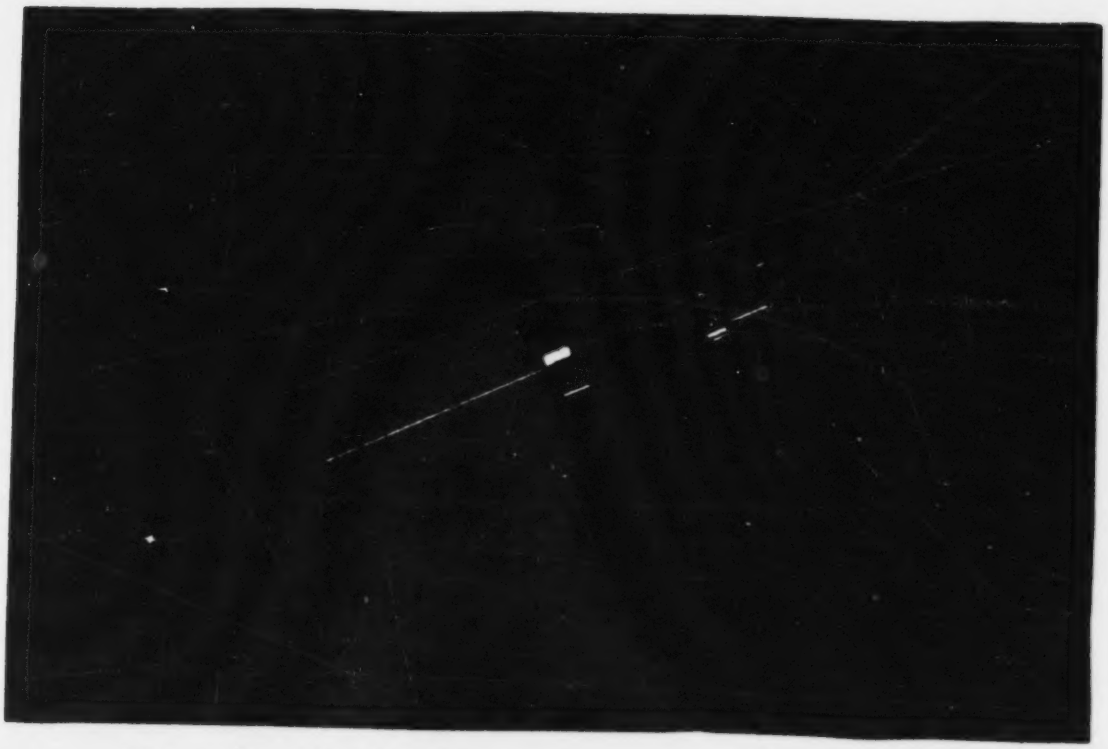
Figure 14 Results of oil/water emulsions



## 4.4. The Wand (or dip type) probe.

Early in the project, we have ordered a Wand (or dip type) probe from Guided Wave, inc. This probe is mainly used with liquid samples. It is designed using a single strand fiber. It employs a mirrored tip to reflect the light from the sending fiber to the receiving fiber. The mirrored tip is gold coated. The distance between the fiber and the mirror is 10 mm. The diameter of the fibers is 320 microns (core diameter). The spectral range of the fibers is from 0.4 microns up to 2.1 microns (25000 $cm^{-1}$ down to 4750 $cm^{-1}$).

After having ordered this probe, it turned out that the pathlength (i.e 20 mm, which is in fact twice the distance between the fiber end and the mirrored tip) was much too long for the samples we were looking at (oil/water emulsions). Those emulsions are so diffusing that there was no radiation coming out of the receiving fiber. However, it seems that Dr. Donini might have an application for such a probe, using less diffusing samples, therefore being able to look at their NIR spectra. See Appendix G for the Wand probe product information.



Picture 7 Wand probe

## 4.5. Reflectance accessory.

A prototype of a fiber optics coupled reflectance accessory has been produced and delivered to Dr. Donini. This prototype helped us understand the critical points that were to be taken care of if ever designing the accessory final version.

The design of this prototype is shown on a rough sketch attached (see figure 15), and its basic operation is as follows. The infra-red radiation which leaves the incoming fiber is focussed on to the center of the sampling cup, where the reflection from the sample occurs. Part of this reflected radiation is then refocussed back to an outgoing fiber and is then guided back to the spectrometer detector.

The optical components we used were standard elliptical mirrors, used in the DA3 Series spectrometer. The long focal length has a value of 8 inches. The small focal length has a value of 1.75 inches. Thus, the magnification factor is:

$$M = \frac{8}{1.75} = 4.6$$

Using this factor, one can compute the illuminated diameter on the surface of the sample, which is:

$$\text{Diameter}_{\text{sample}} = M * \text{Diameter}_{\text{fiber}}$$

$$= 4.6 * .25 \text{ mm} = 1.2 \text{ mm.}$$

The solid angle of collection as seen by the outgoing fiber can also be computed, and it gives a value of:

$$\Omega_{\text{collection}} = \frac{\Omega_{\text{fiber}}}{M} = \frac{0.140 \text{ sterad}}{4.6} = 0.030 \text{ steradian.}$$

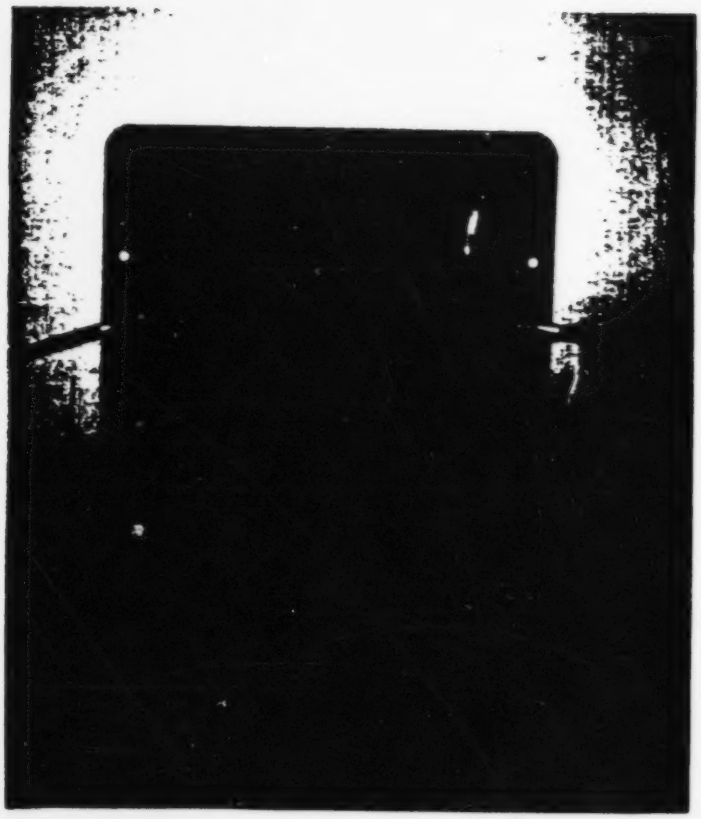
Thus, the efficiency of collection can also be computed. The starting assumption is that the radiation is reflected on a $2\Pi$ steradian, with an efficiency of 100% (no absorption by the sample). This then gives:

$$\text{Efficiency of collection}(\%) = \frac{\Omega_{\text{collection}}}{2\Pi} * 100$$

$$= \frac{0.030}{2\Pi} * 100 = 0.48\%$$

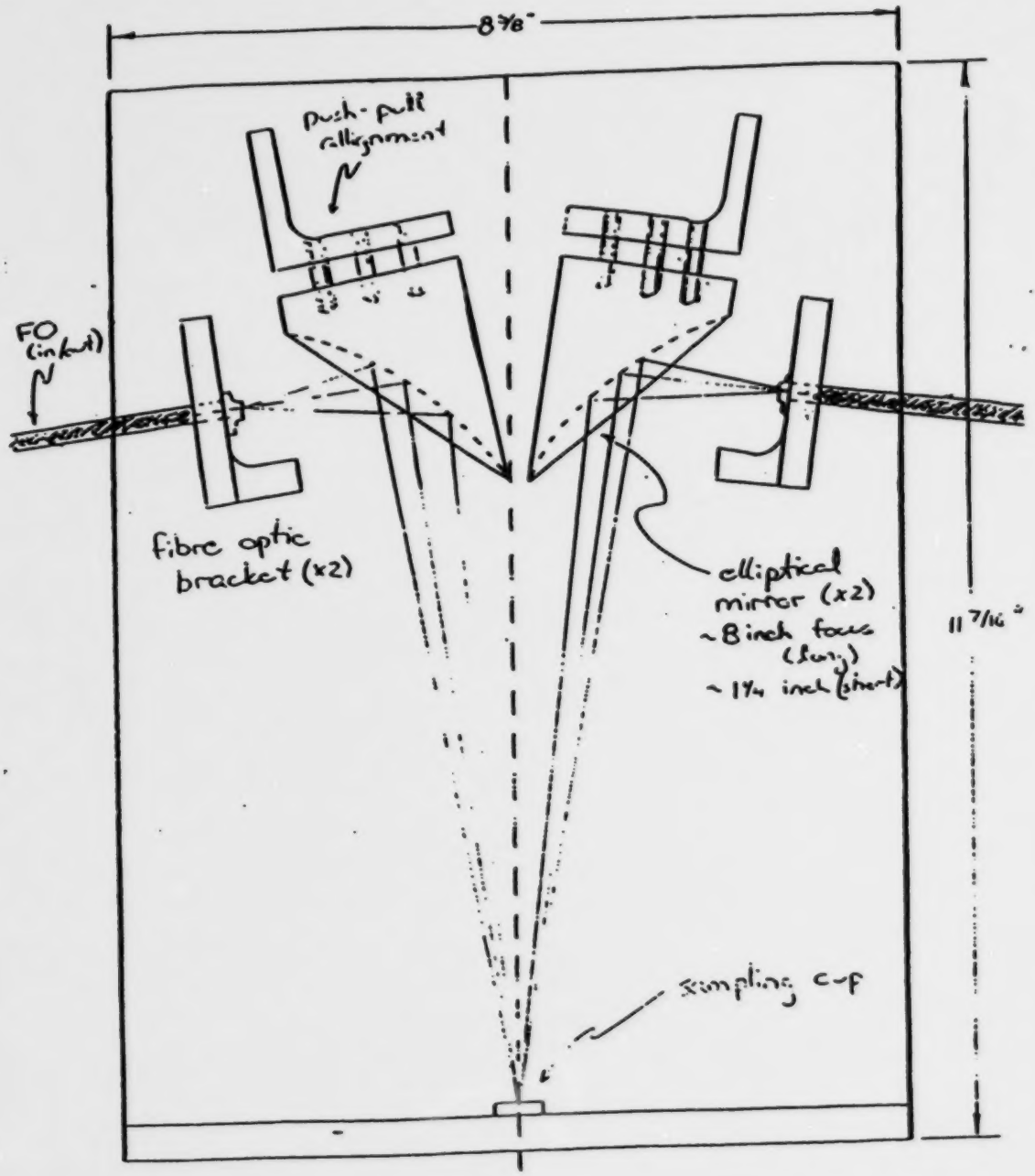
| Efficiency of collection(%) ≅ 0.5% |
|---|

This very low efficiency could explain the poor results we have obtained using this accessory. So the conclusion is that this accessory is not presently well suited for performing NIR reflectance spectroscopy.



Picture 8 Reflectance accessory

Figure 15 Reflectance accessory schematic



# 5. SPECIFICATIONS

## 5.1. Spectrometer

Principle:

Continuous scan Michelson interferometer, employing proprietary "wish-bone" scan mechanism and corner cube mirrors.

Spectral resolution:

Selectable from 1 to 128 $cm^{-1}$ by steps equal to the powers of 2 for Mid IR system. For NIR systems, the highest resolution available is 2 $cm^{-1}$.

Housing:

Cast aluminum, sealed and desiccated, measuring 56 cm (22 1/8 in) wide by 49 cm (19 3/8 in) deep by 19 cm (7 3/8 in) high.

Source:

Quartz halogen lamp with life-time of 5000 hours and temperature of 2900 $^{o}K$.

Beamsplitter:

Proprietary $CaF_2$ design.

Wavenumber Range:

14300 $cm^{-1}$ to 2200 $cm^{-1}$.

Stability:

0.1% standard deviation at 4000 $cm^{-1}$, for ratioed consecutive open beam spectra.

Wavenumber Precision:

0.01 $cm^{-1}$ controlled with an internal HeNe laser.

Measurement:

Adjustable from 1 complete scan (1.25 seconds when using either a MCT or InSb detector, 6 seconds when using a DTGS detector) to infinity, at a spectral resolution of 4 $cm^{-1}$.

Detectors:

The detectors provided with the system are: 1 millimeter liquid Nitrogen cooled InSb detector (dewar holding time of 12 hours) with spectral range from 1800 $cm^{-1}$ to 8500 $cm^{-1}$; 1 millimeter Ge detector at room temperature with spectral range from 5555 to 12500 $cm^{-1}$; 0.5 millimeter InGaAs detector at room temperature with spectral range from 5880 to 12500 $cm^{-1}$ and 1 millimeter Si detector at room temperature with spectral range from 9000 to 14300 $cm^{-1}$.

Sensitivity:

Is a function of detector type and size, beamsplitter type and spectral resolution.

Data Digitalization:

Low noise 16 bit analog to digital converter.

Data Acquisition:

Bidirectional with automatic ZPD detection using laser fringe counting; automatic scan error detection and rejection.

Operating Temperature:

$5^{o}$ - $35^{o}C$.

Built-In Diagnostics:

Automatic systems self check.

Power Requirements:

115/230 VAC, 50/60 Hz, 140 VA.

Weight:

43kg.

## 5.2. Specific Characteristics

### 5.2.1. Fiber Optic Coupling Compartment

Top Plate:

Black-anodized Aluminum; dimensions are 46.3 cm wide ( 18 1/4 in) x 35.6 cm deep (14 in) x 1 cm thick (3/8 in).

Fiber Compartment Cover:

Removable Aluminum cover with a chemically resistant polyacrylic overcoat; exterior dimensions are 37.3 cm wide (14 5/8 in) x 27.7 cm deep (11 3/4 in) x 19.3 cm high (7 1/2 in).

Purge

Dry air or nitrogen gas inlet supplied (standard).

Fiber Alignment:

The alignment is performed by two (2) XYZ stages; the first stage is used to align the fiber transmitting the infrared energy from the interferometer to the sample accessory (OUTPUT Fiber), and the second one is used to align the fiber transmitting the infrared energy from the sample accessory back to the interferometer detector (INPUT Fiber).

### 5.2.2. Remote Sample Plate for Laboratory Purposes

Sample Plate:

Black-anodized Aluminum; dimensions are 33.65 cm wide (13 1/4 in) x 23.5 cm deep (9 in) x 1 cm thick (3/8 in). The two parabolic mirrors interface with the fibers to provide a collimated beam in which the laboratory accessories can be introduce.

Fiber Alignment:

Computer-aided with real time interferogram amplitude display. The alignment is performed using the two XYZ stages holding the optical fibers. For best result, the signal must be optimized each time the accessory is changed.

### 5.2.3. Signal to Noise Test:

*Open Beam S/N Ratio attained on a Transmittance at 4 $cm^{-1}$ resolution in 1.25 s observation time with an InSb, Ge and Si detectors,and 6 s for the InGaAs detector with 1 meter of ZrF fiber in closed loop.*

| Detector Type | Detector Size (mm) | S/N | Spectral Range ($cm^{-1}$) | Range for S/N tests ($cm^{-1}$) |
|---|---|---|---|---|
| InSb | 1 | 900:1 | 2000 to 8000 | 4250 to 4350 |
| Ge | 1 | 700:1 | 5555 to 12500 | 7550 to 7650 |
| InGaAs | 0.5 | 1200:1 | 5880 to 12500 | 7750 to 7850 |
| Si | 1 | 260:1 | 9000 to 14300 | 10050 to 10150 |

Table 7 S/N Test with 1 meter of ZrF fiber

*Open Beam S/N Ratio attained on a Transmittance at 4 $cm^{-1}$ resolution in 1.25 s observation time with an InSb, Ge and Si detectors,and 6 s for the InGaAs detector with 60 meters of ZrF fiber in closed loop.*

| Detector Type | Detector Size (mm) | S/N | Spectral Range ($cm^{-1}$) | Range for S/N tests ($cm^{-1}$) |
|---|---|---|---|---|
| InSb | 1 | 260:1 | 2000 to 8000 | 4250 to 4350 |
| Ge | 1 | 200:1 | 5555 to 12500 | 7550 to 7650 |
| InGaAs | 0.5 | 590:1 | 5880 to 12500 | 7750 to 7850 |
| Si | 1 | 22:1 | 9000 to 14300 | 10050 to 10150 |

Table 8 S/N Test with 60 meters of ZrF fiber

## 5.3. Options

### 5.3.1. Interferometer purge

The user must provide a supply of low pressure dry air (to get rid of water vapor) or dry Nitrogen (to get rid of both water vapor and Carbon dioxide). It includes a swage-lock type inlet gas connection and an open outlet. The flow rate must be controlled by an external valve provided by the user. In routine operation, a steady flow of 0.1 liter per minute is recommended.

When this option is used at the recommended flow rate of dry Nitrogen, absorption by $CO_2$ and $H_2O$ in that part of the optical path which is inside the interferometer housing will not be detectable on the instrumental response (referred to as the Reference spectrum in the Bomem software).

### 5.3.2. DSP-100 interface board

This co-processor board occupies one slot in the AT-type host micro-computer. It replaces the standard interface board supplied with the basic standard system (part SEQ01G). It accelerates the mathematical transformation of interferograms into raw spectra (fast Fourier transforms and phase correction). When used in conjunction with a 80286-based micro-computer equipped with a 80287 co-processor, this option permits the display on screen of a raw spectrum within 4 seconds from the end of interferogram acquisition, at a spectral resolution of 4 $cm^{-1}$. This represents a five-fold acceleration from the basic system coming with the standard SEQ01G interface board.

The DSP-100 board also accelerates the data processing when operating at other spectral resolutions. Typical display times from the end of acquisition are 2 seconds at 8 $cm^{-1}$ and 10 seconds at 1 $cm^{-1}$.

## 5.4. Bomem Easy software general specification

Includes menu driven software, instrument control and data acquisition, spectral display with a maximum of four spectra simultaneously displayed, x and y axes expansion, peak find, solvent subtraction, baseline correction, quantitative analysis, Kubelka Munk normalization, deconvolution, A or % T display, conversion from A to %T and from %T to A, plotting capability, DOS applications call, printing capability, JCAMP-DX interface, learn and macro mode, and software personalization settings.

## 6. CONCLUSION

The main goal of the project was to develop a fiber optics coupled FT-NIR spectrometer. The intended application was to monitor quantitatively the water content of oil/water emulsions. To do so, BOMEM had to provide with the spectrometer some fiber optics coupled accessories, each of them underlying a different sampling technique.

The spectrometer BOMEM designed is one of the best FT-NIR instrument ever produced on the market. Indeed, the standard design of the Michelson MB Series, well renown for its ruggedness and its vibration proof design, has been enhanced by the presence of state-of-the-art beamsplitter, retroreflectors and detectors, combined to a high quality Quartz-Halogen source. This enhancement translates into a shift of the spectral range towards shorter wavelengths (Near IR), without degrading the high modulation level of the interferometer.

By designing the fiber optics interface, BOMEM has significantly increased its knowledge in a field that could become a future niche market for the company. BOMEM is thus now in a good position for offering this kind of system on the commercial market.

The fiber optics coupled accessories that were delivered with the system should be seen as a first step towards the development of commercially available fiber optics coupled accessories. Thus, those will probably need to be upgraded or modified before they can become part of a fully integrated system. Nevertheless, a few of them, mainly the Transmission Cell, the Evanescent Wave Sensor (Cladless Sapphire fiber) and the Wand probe might prove to be very useful in determining more completely the design criteria of the next generation of fiber optics coupled accessories. Concerning the ATR accessory (Tunnel Cell) and the Reflectance accessory, those two will have to be improved before any real work can be done with them.

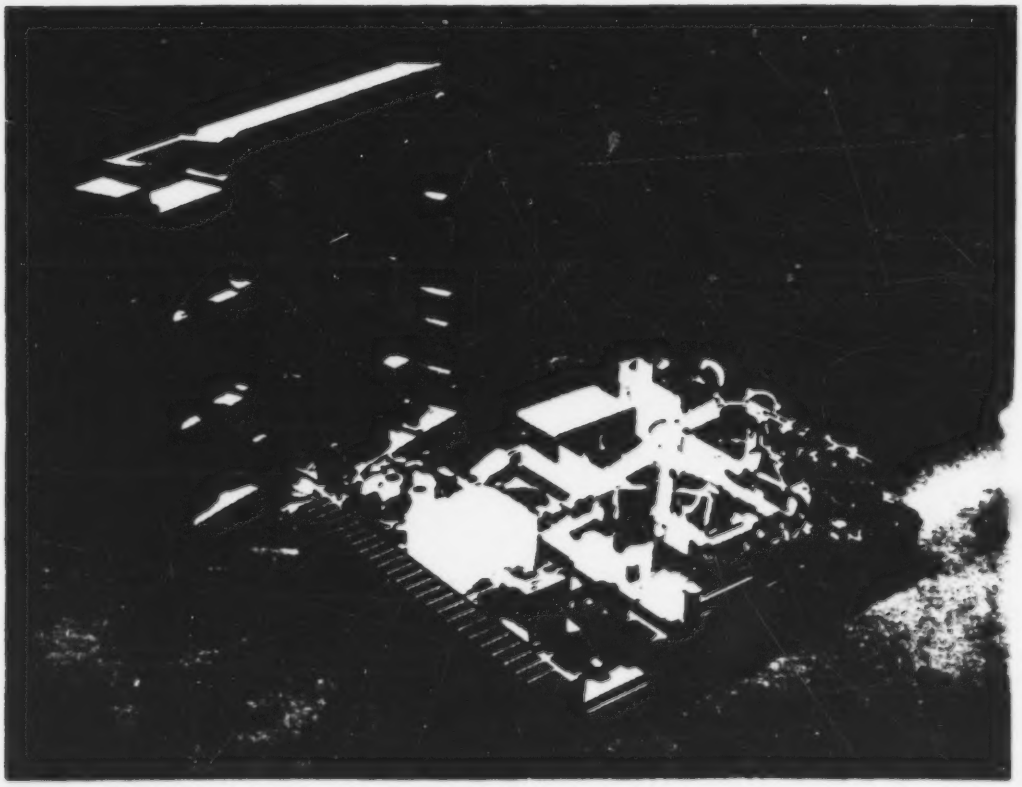
Even though BOMEM considers this project as a success, it nevertheless realizes that there are still points to be addressed before an effective process/quality control system based on NIR characteristics may be fully implemented into an industrial environment. The fiber optics coupled NIR instrument and accessories that were delivered by BOMEM is the first component of such a fully integrated system. Since the delivered system is only part of a final process/quality control system, it is thus required that a research consortium be established. It would then explore some of the remaining problems posed by the introduction of NIR to industrial situations. Discussions between CANMET and interested companies have already begun, and BOMEM has already accepted to participate in such a scientific task force.

# APPENDIX A

## Spectrometer Technical Notes

# The MB Series FT-IR Optical Design from Bomem, Inc.

Daniel Lamarre, Eng. and Frederick Baudais, PhD; Bomem, Inc.



BOMEM

## Introduction:

The heart of any FT-IR spectrometer is the interferometer. Figure 1 shows the path of the infrared radiation inside the MB Series Michelson interferometer.

The incoming collimated beam from the internal IR source hits the lower portion of the beamsplitter at a 45° angle. The transmitted and reflected beams hit the lower halves of the hollow cube corner retroreflectors and the return beams are shifted upward because of the reflections inside the cube corners. The beam then recombines in the upper portion of the beamsplitter. Two beams exit the interferometer, one at 90° to the incoming source radiation (output beam A) and one back to the source but displaced vertically (output beam B).

In single beam instruments like the MB 120, only one beam (output beam A) is directed through the interferometer compartment window to the sample compartment and then onto the IR detector as shown in Figure 2.

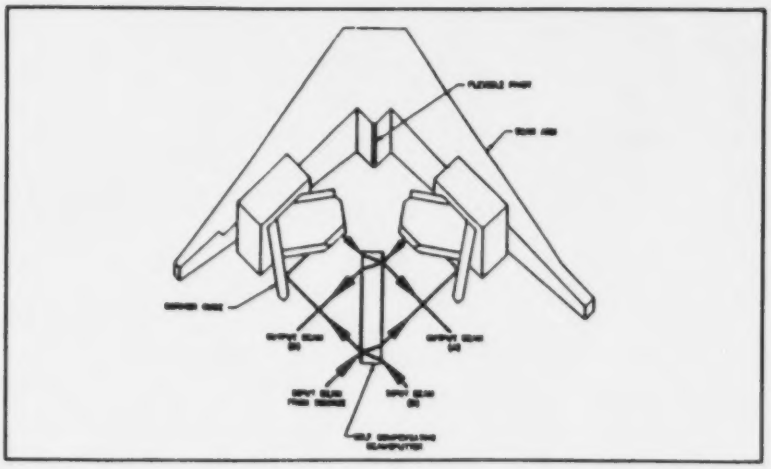


FIGURE 1
Light Path Inside the MB Series Michelson Interferometer

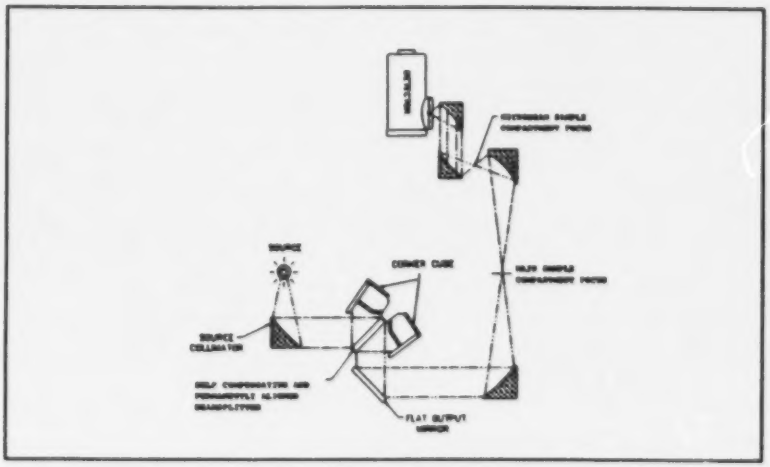


FIGURE 2
Optical Layout of the MB120
FT-IR spectrometer

## Self Compensating Beamsplitter

The common configuration of a Michelson interferometer shown in Figure 3a uses a compensator plate to equalize the amount of

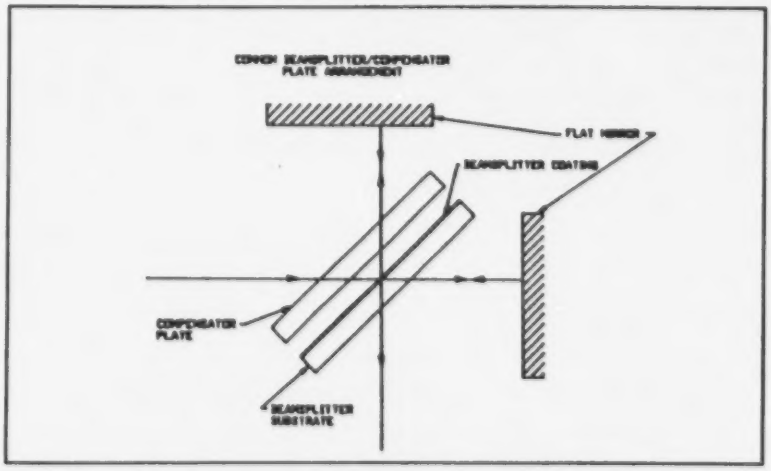



FIGURE 3a
Common Beamsplitter /
Compensator Plate Arrangement

beamsplitter material that each beam in the interferometer arm passes through. In this design, each beam undergoes 4 passes through the compensator and beamsplitter substrate material. At each interface, reflection losses occur which lower the overall efficiency of the interferometer system.

The design of the M and MB series interferometer is shown in Figure 3b. Here the IR beam in each arm undergoes the same number of passes through the beamsplitter substrate material. This design eliminates the need for a compensator plate and minimizes the reflection losses in the system, thus increasing the overall efficiency of the interferometer.

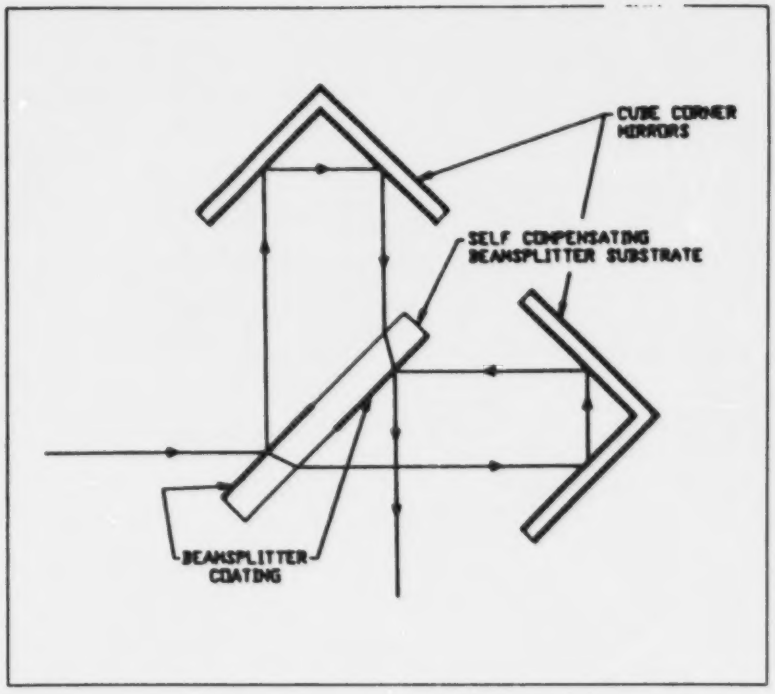



FIGURE 3b
Michelson Series
Self-Compensating Beamsplitter Arrangement

## The Interferometer Module

The interferometer in the MB series (Figure 4) is modular. The scan arm, cube corner retroreflectors, interferometer, white light source, laser, laser power supply and laser detectors are combined into one prealigned module within the spectrometer housing.

This modularity in the design allows for fast and easy repair, if needed, by replacement of parts on the module or by replacement of the prealigned interferometer module itself.

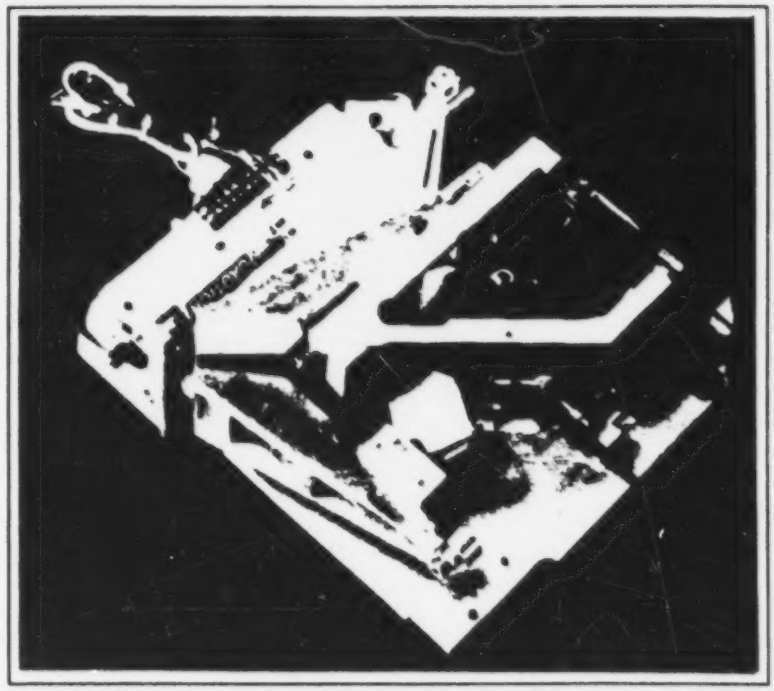


FIGURE 4
Michelson Series Interferometer Module

## Synchronization and Controls

Digitization of the interferogram requires precise monitoring of the optical path in the interferometer. Like most commercial FT-IR spectrometers, the MB series spectrometer incorporates in its interferometer module an internal He-Ne laser emitting at 15798 $cm^{-1}$. Figure 5 shows the travel of the HeNe laser inside the interferometer. This monochromatic laser radiation gives a sinusoidal interferogram which is detected and digitized to yield an optical path difference feedback. Conversion of the infrared signal from analog to digital is triggered at the zero crossings of the laser fringe signal.

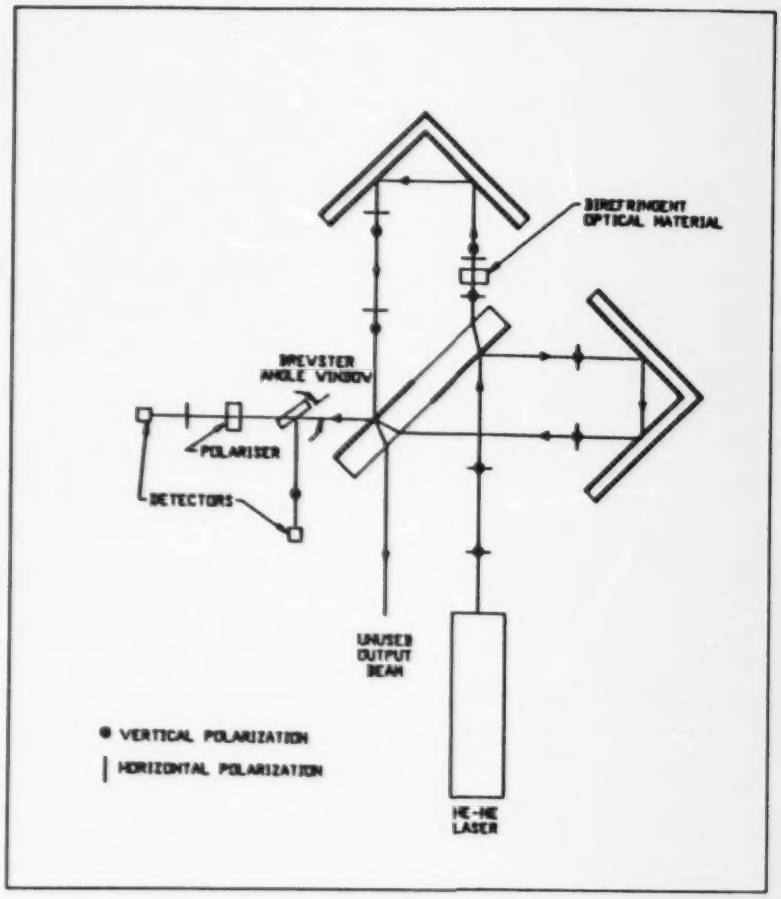



FIGURE 5
He-Ne Laser Light Path within the Michelson Series Interferometer Module

However, a single laser signal is not enough. First the direction in which the scan arm is moving needs to be detected in order to correctly monitor and control the optical speed of the interferometer. Second, the laser signal itself does not give a reference point from which the location of the zero path difference can be determined.

To solve the first problem, quadrature laser signals are used to find the scanning direction. Figure 5 schematically shows what happens to the incoming laser beam. The incident beam is randomly polarized and can then be seen as two different but colinear beams, one horizontally polarized and one vertically polarized. The beams are separated and recombined in the interferometer much like the infrared beam, but in one of the arms, the beams are transmitted through a special birefringent optical material. The index of refraction of this material has the interesting characteristic of giving a different optical retardation for the horizontally and vertically polarized beams. This means than an optical path difference is introduced between the two polarizations. At the output of the interferometer, these two polarizations are separated from one another and directed to different detectors. If one monitors the laser intensity at these two detectors, one sees that there is a shift between the two observed sinusoidal waveforms. Waveform A and B in figure 6 represent the intensities measured at the two laser signal de-

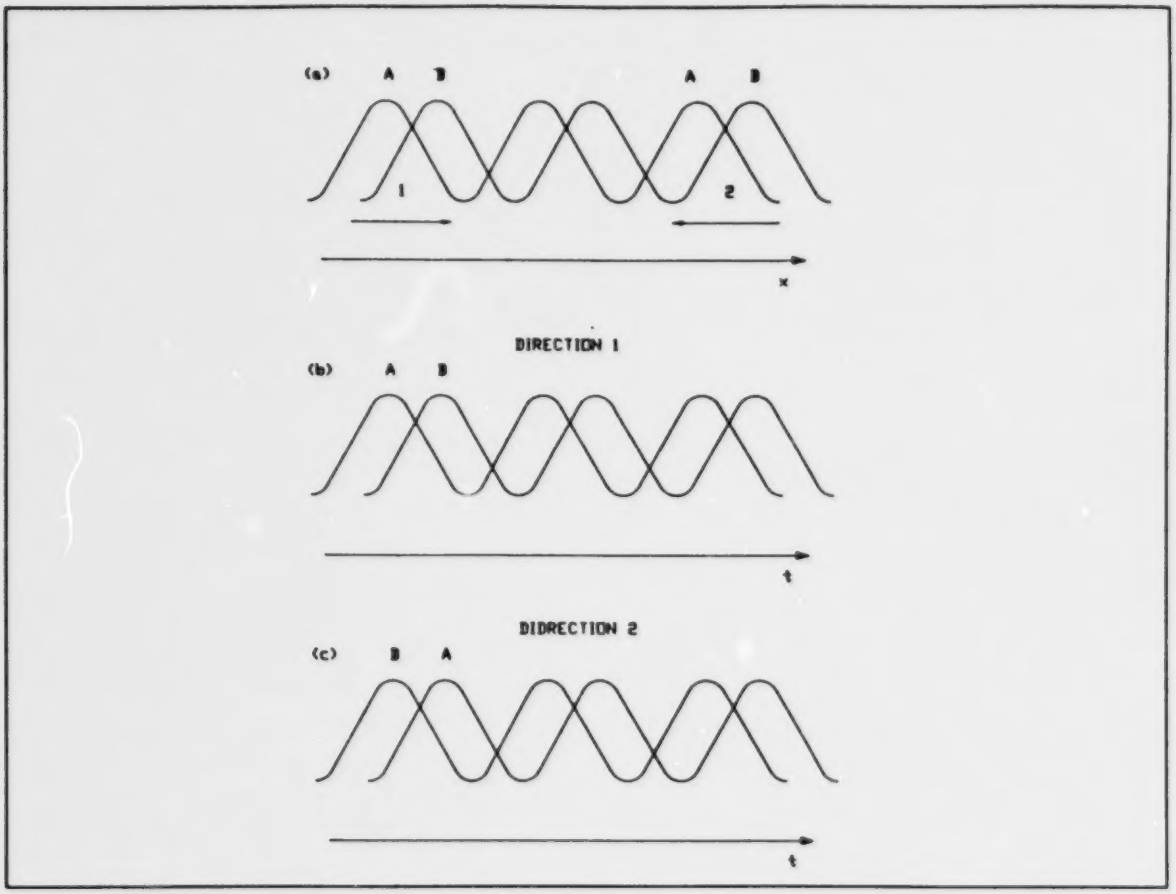



FIGURE 6a, 6b, 6c
Laser Signal Intensities Measured in Direction 1 and Direction 2

tectors as a function of optical path difference. If the optical movement has the direction of arrow 1, waveform A will appear to be leading on waveform B as shown in Figure 6b. If the optical speed has the direction of arrow 2, it is now waveform B that leads A as shown in Figure 6c. The digital electronics recognizes the relative phase relationship generated by moving the mirrors in direction 1 or direction 2 and can determine direction from these two signals. This logic is rigorous. Millions of scans can be executed without a single fringe count error.

The second problem, necessitates some kind of reference in order to find the reference point for the interferometer, the zero path difference location. This is done with a temporary white light system. Each time the MB spectrometer is turned on or when excessive vibrational forces cause the unit to reset itself, a small visible source (light bulb) is lit whose radiation goes through the interferometer using the portion of the beamsplitter that the laser beam uses. The detected white light interferogram is a sharp spike because of the high optical frequency content and broadband emission of the visible source. This signal is detected and used to determine the position of the zero path difference. Once the system has identified this location, the white light source is turned off until the system is reset again.

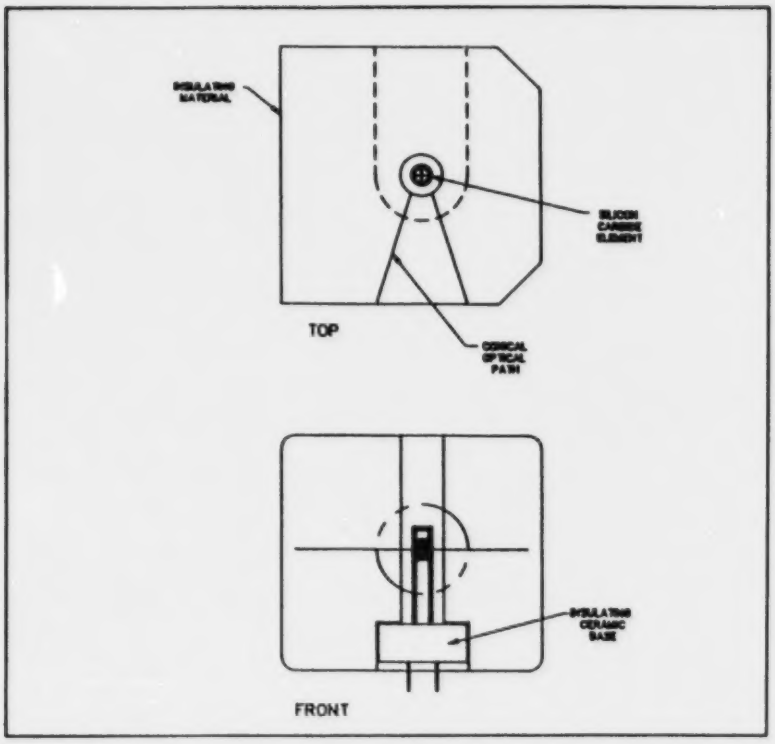



FIGURE 7
Infrared Source and Thermal Housing

## The Infrared Source

A schematic of the mid infrared source inside the MB unit is depicted in Figure 7. The source is made of silicon carbide that when heated by a constant power source to 1100 °K emits broad band IR radiation.

In the MB series design, the source is surrounded by insulating material which reduces the power consumption to the point where no active cooling is required. Neither fan nor water circulation is necessary, the unit being cooled by radiative and natural convection cooling only.

Although there is a source access port in the spectrometer housing, when run under these conditions, the source lifetime is greater than 2 years of continuous operation.

## Conclusion

The MB series interferomter is highly modular, prealigned, incorporates the latest development in optical design: a self compensating beamsplitter design; cube corner retroreflecting mirrors; generation of four independent interferograms, the infrared interferogram, the horizontally and vertically polarized laser interferograms, and the white light interferogram; utilization of an internal HeNe laser for scan velocity control, scan direction sensing via quadrature detection, and digitization control; and a high intensity and long lasting ceramic IR source. All these features make the MB Series one of the most reliable FT-IR spectrometers available.

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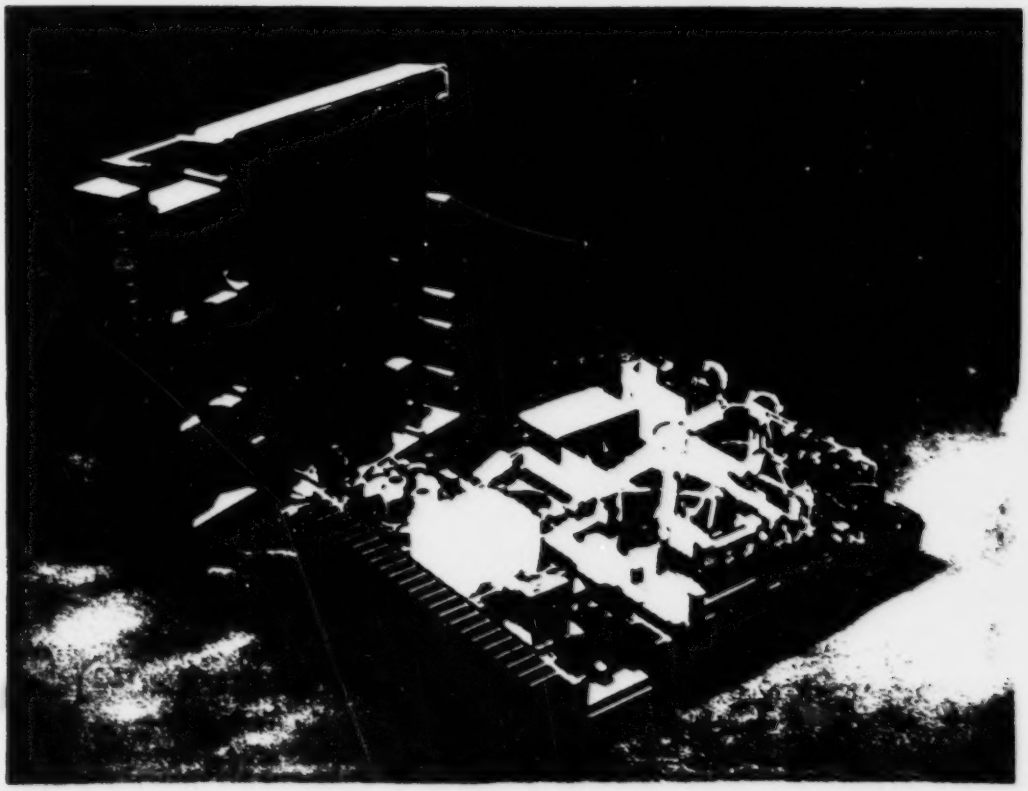
Telex: 40845 BOMEM NL

BOMEM

# The MB Series FT-IR Mechanical Design from Bomem, Inc.

Daniel LaMarre, PE and Frederick Baudais, PhD; Bomem, Inc.



BOMEM

## Introduction

The mechanical design of an interferometric spectrometer is crucial to its operation. Both sensitivity to external stresses, and performance stability can be affected by the system's mechanical design.

## MB Series Interferometer Mechanical Design

Figure 1 is a photograph of the patented interferometer module for the MB Series. The mechanical components consist of the scan arm, and the support module.

## The Moving Scan Mechanism

The scan arm holding the cube corner retroflectors is rigid, symmetric and balanced so that its center of gravity lies at the scan pivot position. This allows the mechanism to be insensitive to orientation and linear accelerations such as common vibrations. As a result, the spectrometer can be oriented either horizontally as in a normal laboratory environment or vertically when it is necessary to minimize the amount of space occupied by the spectrometer as in many industrial environments. Also it can be operated in environments having substantial vibrations.

Scan arm inertia has been minimized by a gradually decreasing cross section going from the pivot position to the cube corner mirrors.

The pivot is made of two steel blades aligned perpendicular to one-another at the top and bottom of the scan arm/support module assembly. This makes possible an essentially frictionless rotational scan arm movement. The dimensions of the pivot blades have been optimized to obtain a very rigid pivot in the axial or perpendicular radial direction but allowing the scan arm to rotate in the horizontal radial direction.

The flexibility of the steel blade is such that the movement required for maximum spectral resolution never exceeds the elastic deformation range of the steel. Under these conditions, the lifetime of the pivot is virtually infinite. Since no friction is present, no wearing occurs. Under normal conditions of vibration and temperature changes, the interferometer will scan smoothly and freely.

The scan arm movement is controlled by a linear motor: a voice coil and a permanent magnet arrangement. Again this motor is frictionless with no parts to wear out. The combination of a frictionless flex pivot bearing with a frictionless scan motor drive mecha-

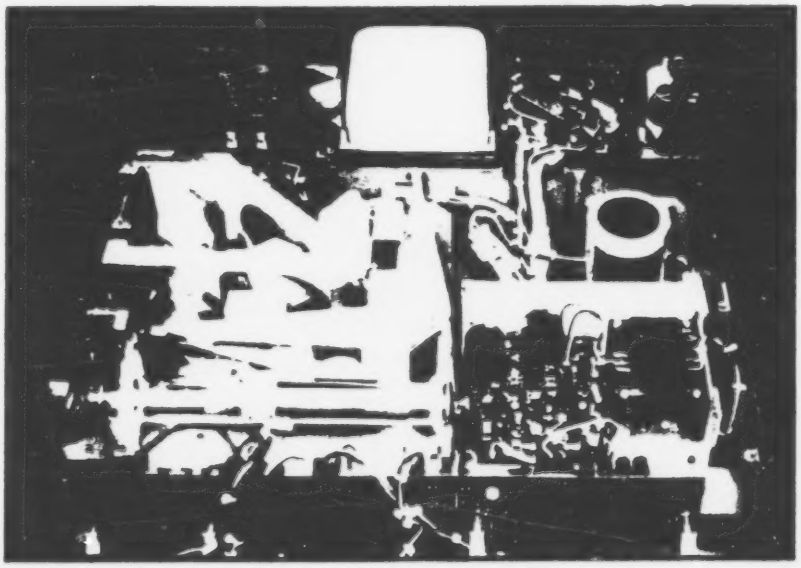


FIGURE 1
Bomem MB Series Interferometer Module

nism result in a scanning operation that is smooth, reliable and dependable over long periods of time.

The scan arm movement is rotary as shown in Figure (2). Both cube corners follow the same arc of travel. In this design, interferometer alignment is maintained by the ability of the cube corners to move exactly together. The rigid cast aluminum scan arm assures that this occurs. The cube corner retroreflectors having the property of maintaining an output beam parallel to the input beam independent of orientation ensures that the recombinant IR radiation from both arms intersects the beamsplitter at exactly the correct position and angle for light interference to occur.

## The Support Module

The support module in Figure (1) supports the scan arm, the self compensating beamsplitter, the HeNe reference laser, the white light source, the quadrature detector module, the permanent magnetic housing for the scan motor, and the HeNe laser power supply.

The support module must be mechanically rigid, show a low sensitivity to temperature changes and at the same time accept all the mechanical and optical components of the interferometer. Mechanical rigidity is achieved by making the support module from a single piece of cast metal whose surfaces are machined at appropriate places. All protruding support mounts have at a minimum two joined sides to ensure mounting rigidity. The metal used is aluminum for an even heat distribution throughout the entire support module. These features allow the interferometer to reach a high degree of stability and to be insensitive to vibration and temperature changes. This is the only interferometer design that does not require optimizing alignment adjustments. It is permanently aligned.

## The Interferometer Housing

The interferometer housing shown in Figure (3) supports the interferometer module, the IR source, the electronic circuit board, and the interferometer module. It also supports power supply internal cabling, and provides access to the internal desiccant chamber.

The housing provides a sealed environment for the interferometer module protecting it from dirt and humidity. It also protects the interferometer from air currents

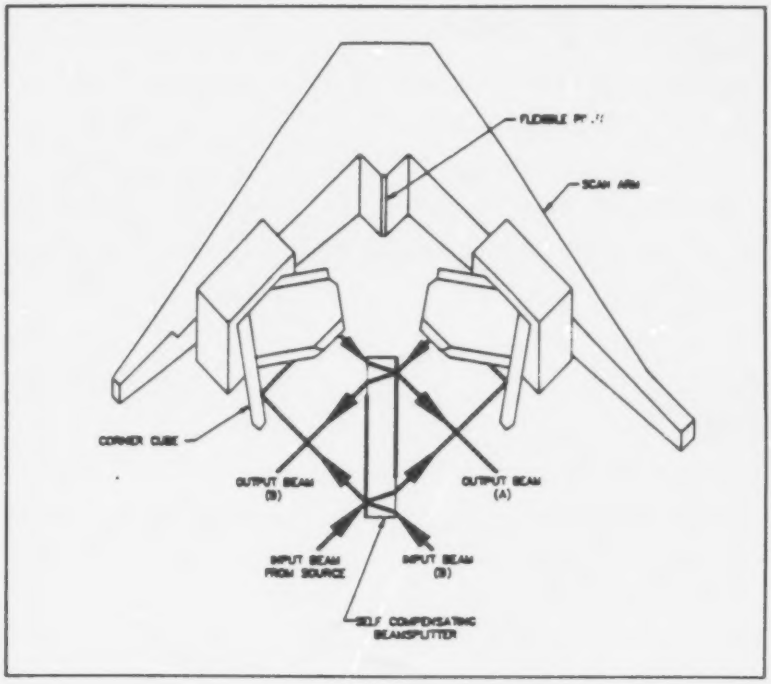



FIGURE 2
Bomem MB Series Scan Arm Movement

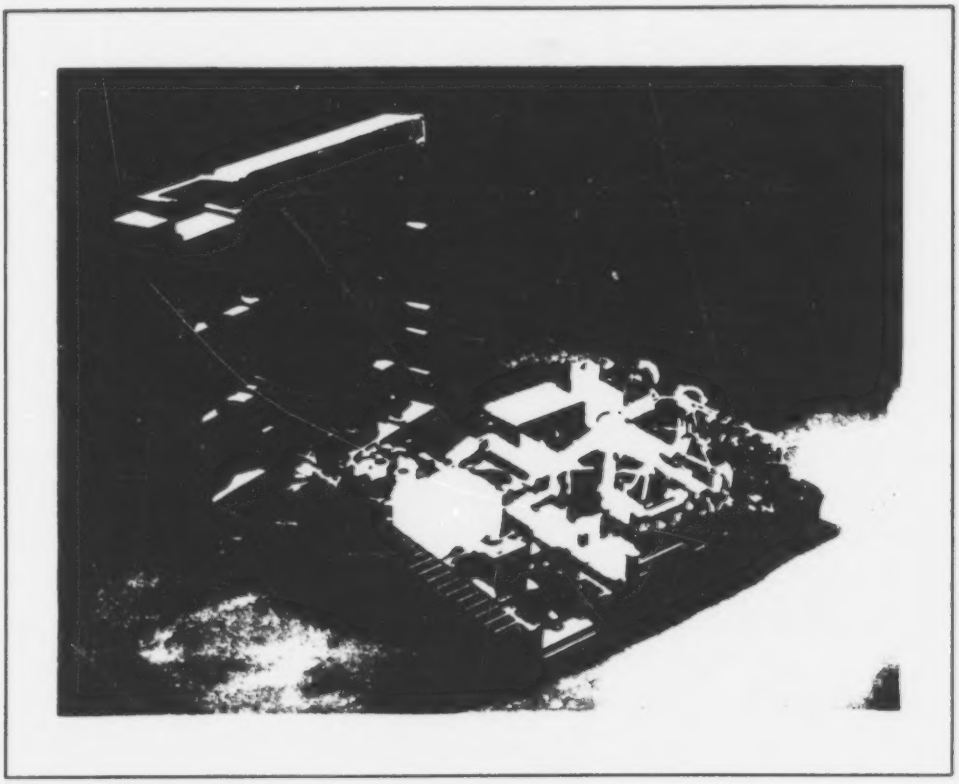


FIGURE 3
Bomem MB Series Sealed and Desiccated Spectrometer Housing

that, if allowed in the arms of the interferometer, would cause intensity instabilities. Finally it allows efficient dissipation and distribution of internally generated heat from the IR source, power supplies and electronics, with neither forced air nor water to the environment, as well as distributing heat from an external source (eg, a hot cell) evenly throughout the spectrometer.

## Conclusion

The patented mechanical design of the interferometer and scan mechanism, the support module and the housing for the MB spectrometer have been highly optimized to provide a durable and reliable spectrometer, insensitive to the external environment in which it is placed providing for the first time an FT-IR without any adjustments.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BOMEM

# APPENDIX B

## Beamsplitter General Specifications

450, St-Jean-Baptiste
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Canada
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Fax: (418) 877-2984

# SPECIFICATION

PIECE NO : 1080092L REV : 1/0

DESC : $CaF_2$ Beamsplitter 2.75" DIA (1200 - 14000 $cm^{-1}$)

PAR : Hervé Guy DATE : January 3, 1989

APP : DATE :

APP :

SPECIFICATION :

Material : Interferometer grade $CaF_2$

Diameter : 2.75 ± 0.01"

Thickness : 0.375 ± 0.01"

Flatness : Both faces optically flat to < $\lambda/10$ ( $\lambda$ = 0.63 µm) over greater than 80 % of central surface. Both surfaces to be polished to low visible light scatter finish.

Parallelism : Both faces parallel to < 1 sec. of arc.

BOMEM

PART NUMBER: IOB0092L REV. 1 – 0

DESC.: $CoF_2$ BEAMSPLITTER MICHELSON

SPECTRAL RANGE: 1200 – 14000 $cm^{-1}$
.72 – 8.33 um

MATERIAL: SEE PAGE 1 OF 2

# COATING SPECIFICATIONS

OPERATING ANGLE OF INCIDENCE: 45 °

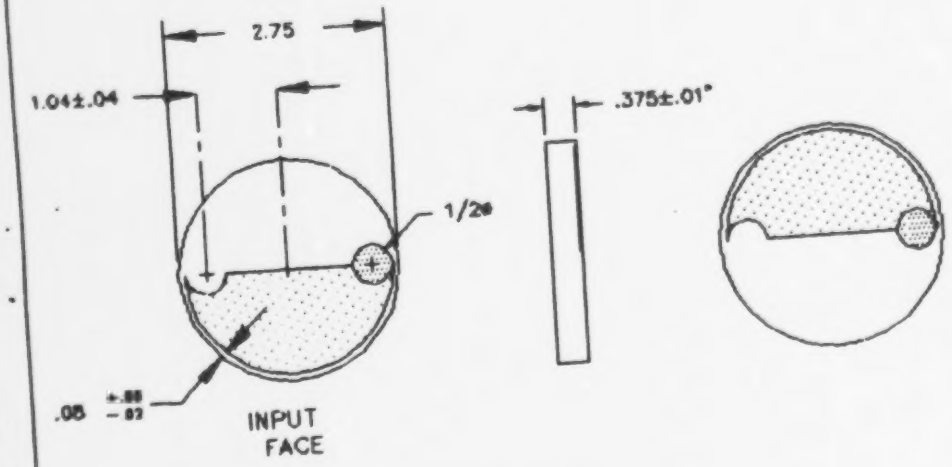
COATING #1:
MATERIAL: $Sb_2S_3$
OPTICAL THICKNESS: $\lambda/4$ @ $\lambda$ = 0.633 um

COATING #2:

FIRST LAYER
MATERIAL: ZnS
OPTICAL THICKNESS $\lambda/4$ @ $\lambda$ = 1.2 um

SECOND LAYER
MATERIAL: ZnSe
OPTICAL THICKNESS $\lambda/4$ @ $\lambda$ = 1.2 um

THIRD LAYER
MATERIAL: Si
OPTICAL THICKNESS $\lambda/4$ @ $\lambda$ = 1.2 um




UNCOATED AREA
COATING #1
COATING #2

| Unless otherwise specified, dimensions are in inches | | |
|---|---|---|
| TOLERANCE | INCHES | mm. |
| | ±1/32" | ±.5 |
| 1 place (.X) | ±.02" | ±.25 |
| 2 places (.XX) | ±.01" | ±.06 |
| 3 places (.XXX) | ±.002" | |
| COATING THICKNESS | | ±10% |

BY: J McK
DATE: JAN 03, 89

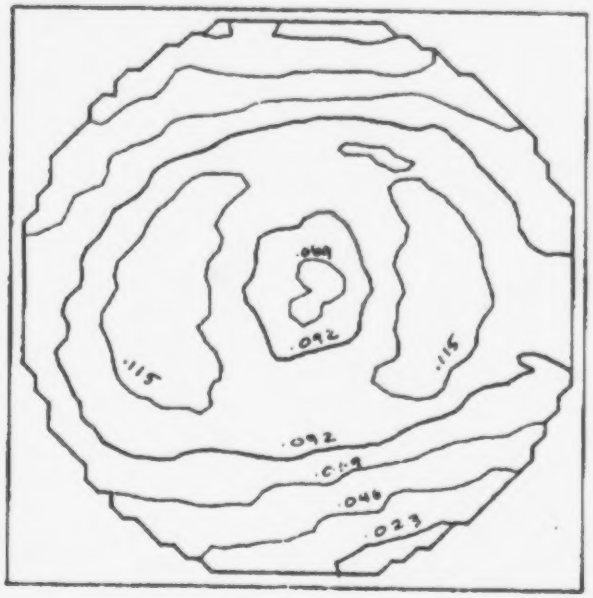
APP.: Wayne Amy
DATE: Jan 25, 89

*** WAVEFRONT ***

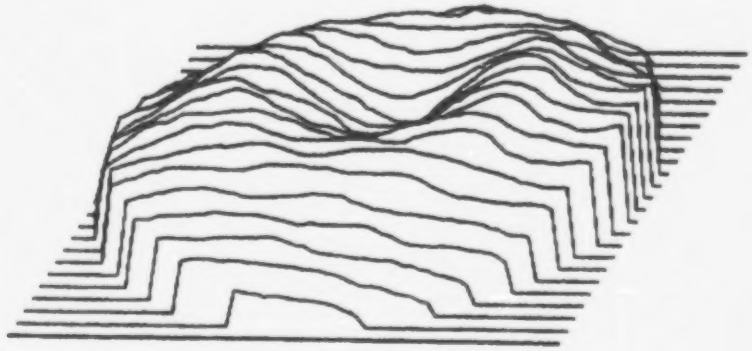
16-MAR-1989/14: 51: 13

| | | |
|---|---|---|
| Part ID | : | BOMEM |
| Serial # | : | IOB0092 |
| Analysis | : | phase |
| F/NO | : | plano |
| Fast | : | off |
| Averages | : | 1 |
| Trim | : | 0 |
| Calibrate | : | ON |
| AGC | : | ON |
| Scale | : | 0.50 |
| Wave Out | : | 0.6328 |
| Reference | : | none |
| Remove | : | TLT |

PV : 0.138 PTS : 9361
RMS : 0.028



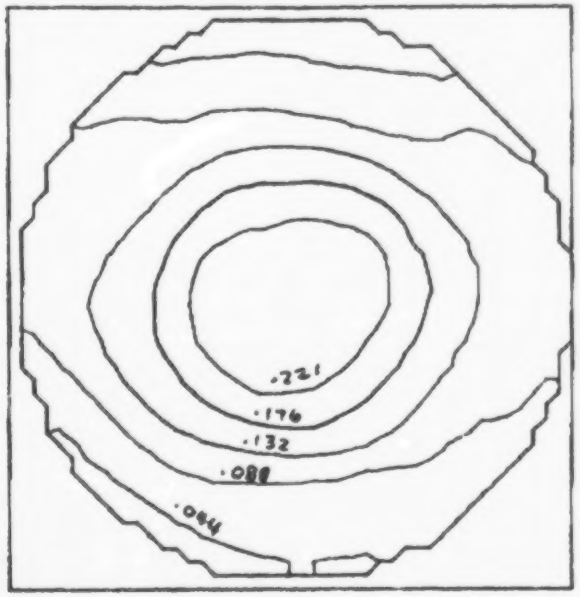

0.115
0.092
0.069
0.046
0.023
no
data



*** WAVEFRONT ***

16-MAR-1989/15: 09: 06
Part ID : BOMEM
Serial # : IOB0092
Analysis : phase
F/NO : plano
Fast : off
Averages : 1
Trim : 0
Calibrate : ON
AGC : ON
Scale : 0.50
Wave Out : 0.6328
Reference : none
Remove : TLT

PV : 0.265 PTS : 9366
RMS : 0.063

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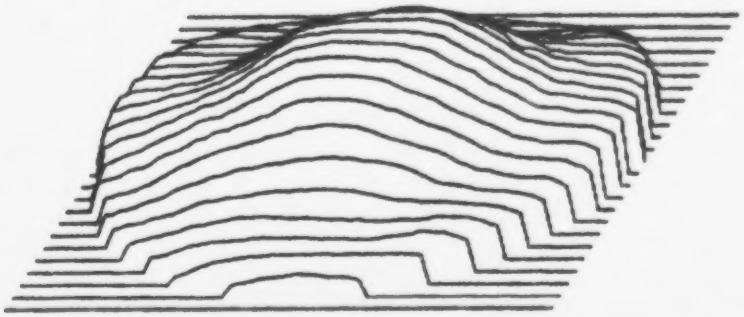
no
data



SIDE 'A'

SIDE 'B'

# APPENDIX C

## Retroreflectors General Specifications

PRECISION
LAPPING & OPTICAL CO., INC.

FAX 516-561-2802
P.O. Box 68, 43 Railroad Ave., Valley Stream, NY 11582 / (516) 561-2770 / Telex 649651 PLOCI VSTM

December 22, 1988

To: Bomem, Inc.

Attn: Jean Giroux

Fax: 418-877-2834

Dear Sir:

We confirm our quote as follows:

Item: 2½" x ½ sec. unmounted Omni-wave Retroreflector
Quantity: 2
Price: For aluminum $900.00 ea.
For gold coating $955.00 ea.
Delivery: 4 weeks ARO
Terms: ½% 10, net 30
Validity: 60 days
F.O.B.: Valley Stream, N.Y.

Thank you for this opportunity to quote.

Very truly yours,

PRECISION LAPPING & OPTICAL CO. INC.

Barry Goodman

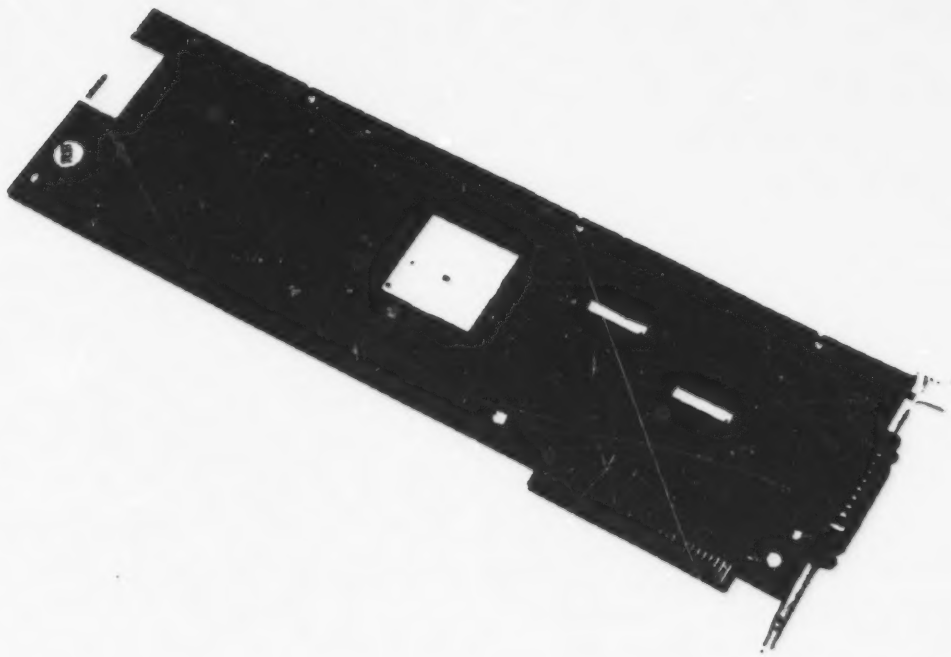
BG:js

# APPENDIX D

## DSP Board General Description

# A New Hi-Throughput FT-IR Interface Card; Description & New Application Opportunities

by P. Beauchesne, C. Lafond and F. Baudais; Bomem, Inc.

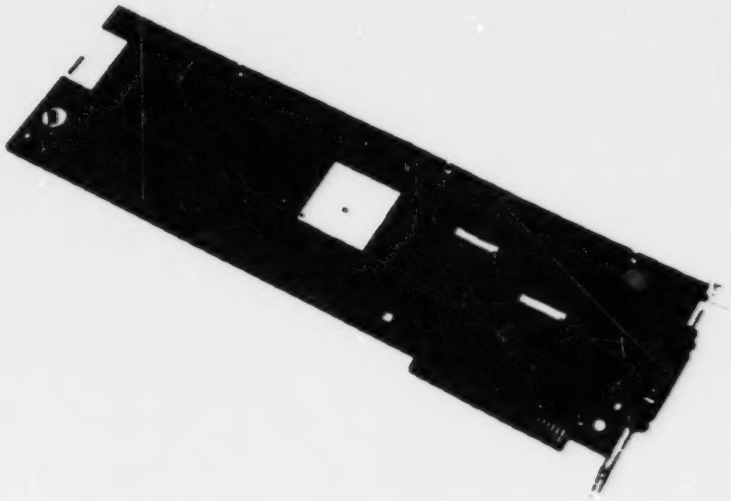


BOMEM

## INTRODUCTION:

The multiplex advantage of FT-IR spectrometers enables them to gather a full high quality infrared spectrum in a fraction of a second. However, the necessary transformation of raw interferograms to usable spectra is very computationally intensive. This Fourier transform step often greatly offsets the FT-IR speed advantage when performed on low cost microcomputer based systems.

In order to reduce this calculation time to nearly zero compared with the computation time on an IBM AT™, Bomem has developed the DSP100 signal processor.



## DSP100 FEATURES:

* Single AT™ Compatible Board
* 10 MIPs DSP56001™ Chip from Motorola
* 64Kb of On-board Fast Static RAM
* Interface to Michelson Series FT-IRs
* Interferogram to 1 $cm^{-1}$ Spectrum in 391 ms

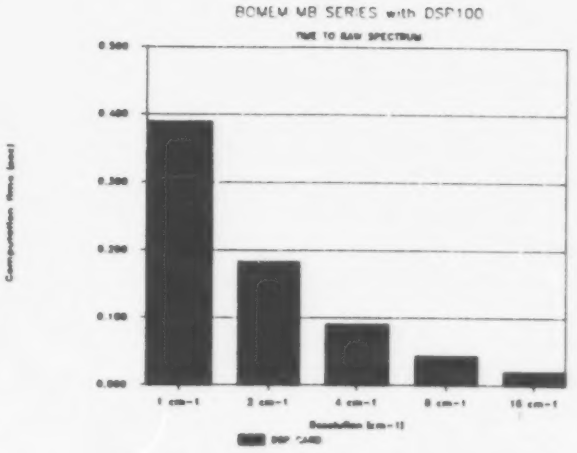
The DSP100 is an IBM AT™ compatible electronic board based on the latest 10 MIPs (mega instruction per second) Digital Signal Processor circuit from Motorola, the DSP56001. With 64Kb of on-board fast static RAM (random access memory), and interfaced to Bomem's Michelson Series spectrometers, it transforms a 32768 point interferogram to a 1 $cm^{-1}$ resolution raw spectrum in less than half a second!... This provides for greatly reduced total time to display.

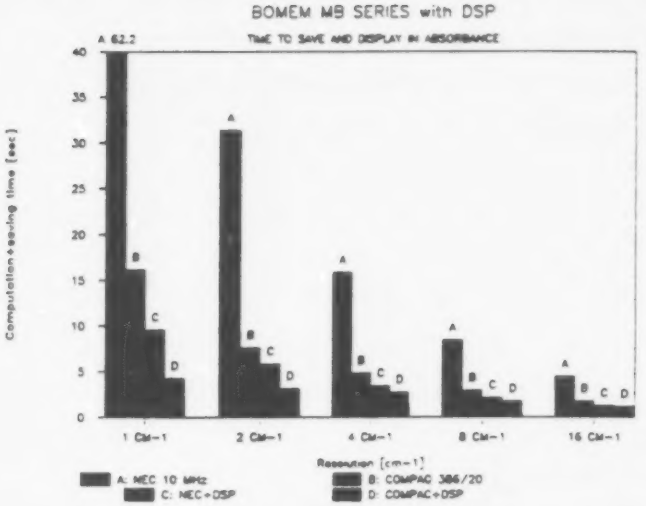
## DSP100 ADVANTAGES:

* Negligible FFT time
* Frees the computer for other tasks
  (e.g. Quant...)
* Faster FFT on AT™ than on 80386
  machines alone
* Low cost

## APPLICATION OPPORTUNITIES:

* Real time process monitoring
* Study of reaction kinetics
* High-throughput quality control
* Better laboratory productivity
* Etc.....



## DSP100 ADVANTAGES:

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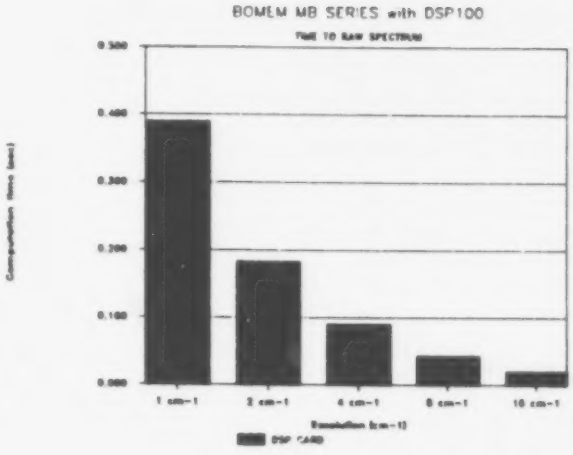
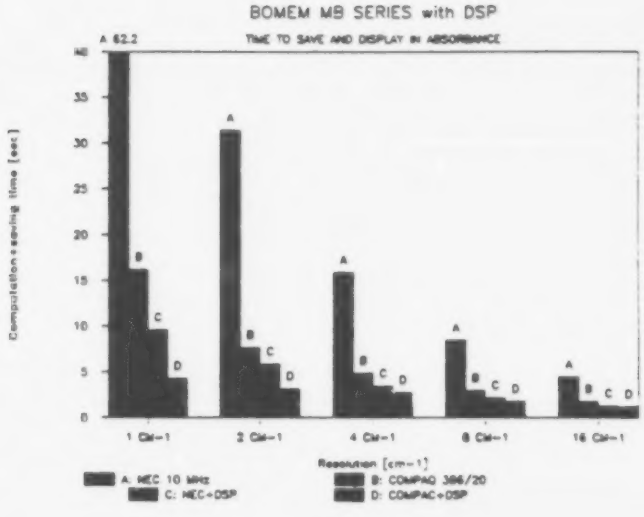
* Real time process monitoring
* Study of reaction kinetics
* High-throughput quality control
* Better laboratory productivity
* Etc.....



## CONCLUSION:

By providing the host AT™ microcomputer directly with a usable spectrum while allowing the microcomputer to perform other tasks, the DSP100 opens new opportunities for real time applications using Bomem's low cost industrial and laboratory Michelson Series FT-IRs.

This is not a unique fast fourier processor. However, it has been designed uniquely by Bomem for FTIR data acquisition, transformation and installation on the 8 bit bus slot of an IBM AT™ or compatible. It provides the elegant combination of fast processing speed and low cost.

IBM and AT are trademarks of International Business Machines.


Bomem Inc. - Home Office
450 St Jean-Baptiste
Quebec (Quebec)
Canada G2E 5S5
Tel.: (418) 877-2944
Fax: (418) 877-2834
Telex: 05143

Bomem Inc. - World Field Operations Center
1360 Wood Dale Road, Suite B
Wood Dale, IL 60191
Tel.: (312) 350-0550
Fax: (312) 350-0780
Sales/Service: 1-800-888-FTIR
Telex: WUI 403252 BOMEM INC

Bomem Inc. - European Office
Bizonspoor 6007
3605 LV Maarssen
The Netherlands
Tel.: 313465.62773
Fax: 313465.63998
Telex: 40845 BOMEM NL


BOMEM

# APPENDIX E

IRIS Product Information

IRIS

# Product Information No. A-250/330

## IRISensor* 250/330

IRISensor 250/330 is one of a family of multispectral near infrared transmitting heavy metal fluoride optical fibers now available in commercial quantities from IRIS FIBER OPTICS, INC.. The material, manufactured using proprietary and state-of-the-art technology under license from British Telecom, offers users outstanding optical performance and mechanical strength -- advantages not previously obtainable in fibers of this type.

### Typical Properties

| | |
|---|---|
| Spectral Transmission Range | 300 nanometers wavelength in the UV to 4.5 microns wavelength in the mid IR |
| Attenuation (loss) | <20dB/kilometer at lowest loss |
| Numerical Aperture | 0.21 |
| Refractive Index | 1.45 TO 1.5 |
| Tensile Strength** | 75,000 psi (minimum) |
| Minimum Bend Radius at Break** | 11 mm |
| Glass Core/Glass Clad Material | zirconium fluoride ((ZBLAN) |
| Glass Core/Glass Clad Diameter | 250/330 microns |
| Protective Coating | epoxy acrylate, approximately 45 microns thick |

IRISensor 250/330 is available for purchase as single fiber, uncabled or cabled, as well as in bundles. Single cabled fiber is terminated with standard SMA connectors and bundles with brass or stainless steel ferrules. Fiber ends are optically polished.

*Trademark of IRIS Fiber Optics, Inc.
**From two point bend test data

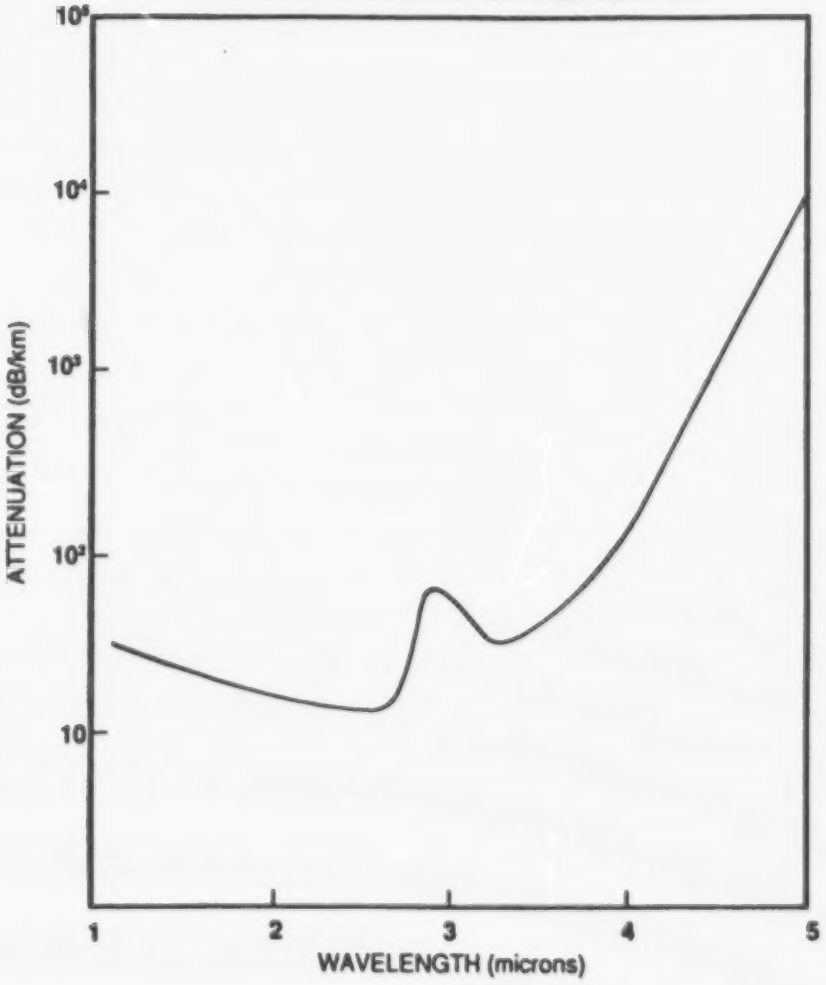
62088

IRISensor 250/330 provides users with a medium core size fiber while maintaining a small bend radius. The fiber will be of interest in a broad range of demanding medical, industrial and military applications, including laser surgery, remote spectroscopy, temperature sensing, and process measurement and control.

IRIS's R & D Department is engaged in application development in a wide range of potential uses for infrared transmitting fibers. Our application engineers are ready to assist you in adapting our fibers to your specific system or application.

**TYPICAL**

**ATTENUATION CURVE FOR IRISensor Fiber**




**FOR ASSISTANCE OR FURTHER INFORMATION:**

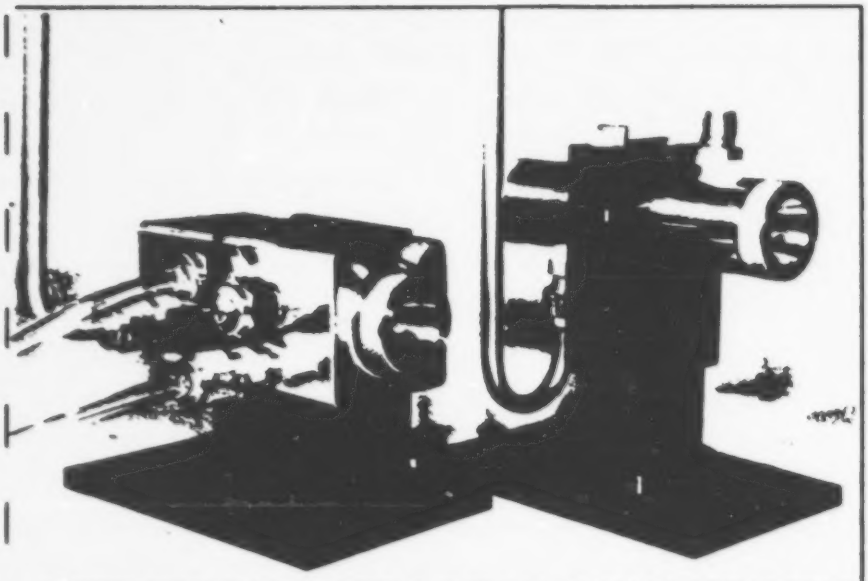
IRIS
INFRARED OPTICS, INC.

40 Nagog Park, Acton, MA 01720 U.S.A. Telephone 508 635 9400 FAX 508 635 9481

Copyright 1988 IRIS Fiber Optics, Inc.

# APPENDIX F

Tunnel Cell Product Information



# FTIR TUNNEL CELLS FOR QUANTITATIVE LIQUID SAMPLING

*A new generation of internal reflectance sampling systems for precise chemical analysis of stationary or flowing liquids... on-line or in the lab*

TNL Series TUNNEL Cells* are the first cylindrical internal reflectance sampling systems to provide the high degree of absorbance linearity and repeatability required for demanding quantitative analysis. The secret is a unique optical design which concentrates the infrared radiation in the internal reflectance element within a very narrow range of incidence angles and thus eliminates the major cause of nonlinearity common to other ATR cells. The result is significantly enhanced absorption, high optical transmission, and unmatched linearity and repeatability.

The TUNNEL Cell design retains the advantages of earlier cylindrical internal reflectance (CIR) cells, including optimum match to the FT-IR beam geometry, advantageous liquid flow characteristics, and the use of highly reliable "O" ring seals. To these it adds outstanding optical performance as well as rugged, adjustment-free construction. These features make the TUNNEL Cell ideal for the most demanding applications.

Several versions of the TUNNEL Cell are available, with models configured for both laboratory and process monitoring applications. Individual models feature sample volumes ranging from 25 microliters (ideal for HPLC detection) to 20 milliliters – as well as capabilities for integral heating and cooling and for operation at pressures to over 1000 psi. Most models employ Axiom's proprietary helical flow geometry which eliminates dead volume, minimizes ATR element abrasion, and maximizes cleaning efficiency. Even highly viscous samples can be analyzed and then rapidly flushed out with no measurable sample retention.

The TUNNEL Cell was designed right from the start to meet the uncompromising requirements of continuous duty on-line analysis. Stainless steel construction, integral permanently aligned optics, self cleaning flow geometries, and integral temperature control are some of the features which insure the high level of reliability needed for process applications.

The high performance features which allow TUNNEL Cells to be used in demanding on-line applications provide valuable benefits for the laboratory analyst as well. Now you can perform true quantitative IR liquid analysis with no need for cell calibration and with absolute confidence in your results.

FEATURES:

- Rugged, adjustment-free design
- Absolute repeatability
- Unmatched absorbance linearity
- Enhanced sensitivity
- Rapid sample cleanout
- Compatible with laboratory and process applications

* Patents Pending

PS -TNL-02(902)

Axiom Analytical INCORPORATED

1278 Glenneyre, Laguna Beach, CA 92651
Tel. (714) 497-1407 FAX (714) 494-1537

## THE TUNNEL OPTICAL DESIGN

The performance limitations encountered with previous cylindrical internal reflectance cells[1] result largely from their use of strongly focussed IR radiation, typically spanning an angular range of 20°, at the input end of the internal reflectance element. This wide range of angles gives rise to a correspondingly wide range of effective sample thicknesses and hence of absorbance sensitivity per reflection. In addition, the rays which are more strongly absorbed at each reflection also experience the greatest number of reflections. These two effects give rise to a very strong dependence of absorption on incidence angle. The result is a marked degradation of absorbance linearity (adherence to Beer's Law analogous to the "wedged cell" effect sometimes encountered in transmission spectroscopy[2]).

The TUNNEL optical design circumvents these problems by concentrating the incident radiation within a narrow range of angles in the cell. The design is illustrated in Figure 1. Although collimated radiation is used in this illustration, the TUNNEL cell will also yield superior performance when operated in a typical FT-IR focussed beam sample compartment.

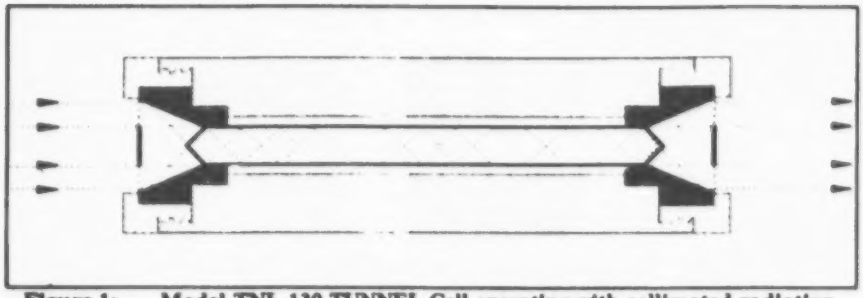


**Figure 1: Model TNL-130 TUNNEL Cell operating with collimated radiation. Repeatability and absorbance linearity are achieved by ensuring that all rays which enter the cell parallel to its axis strike the interface between the element and the analyte at the same angle (in this case, 45°). The optical stops at each end block rays which would enter the element without first striking the reflecting cone.**

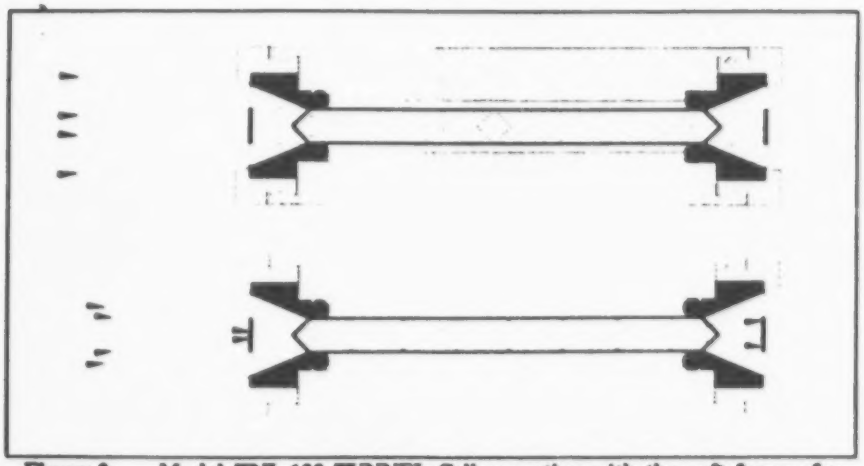


**Figure 2: Model TNL-130 TUNNEL Cell operating with the soft focus of a typical focussed beam sample compartment. As in the collimated case, the TUNNEL optical design maximizes the effective collecting aperture while minimizing the angular distribution of rays within the internal reflectance element. Figure 2a illustrates the extreme rays which pass through the cell. Figure 2b illustrates the function of the stops in eliminating rays which would otherwise pass through the rod without first striking the input reflecting cone.**

In common with the previous cylindrical internal reflectance devices, the TUNNEL Cell employs a circular cross section element with 90° polished conical surfaces at each end. Compared to designs employing rectangular crystals, this approach has several advantages, including: ease of sealing, optimum liquid flow geometry, and optimum match to the circular cross section of the FTIR optical beam. Unlike previous designs, however, the TUNNEL design does not use focussing optics to concentrate the radiation on the crystal. Instead, it uses a reflecting cone to redirect the input radiation so that each ray strikes the conical rod surface as close as possible to normal incidence. A second cone intercepts and redirects the rays leaving the crystal.

The TUNNEL Cell optical design provides unprecedented data repeatability. This is a result both of the inherent linearity of the cell's operation and of a unique structure which mechanically fixes the relationship between the crystal position and the various optical elements. The conical reflectors which direct the radiation into the element are integral to its support. No misalignment can take place. As a result, a given TUNNEL Cell will provide the same results run after run, making true infrared quantitative analysis of liquids a reality.

## OPTIMIZED LIQUID FLOW GEOMETRY

Most TUNNEL Cell models employ Axiom's proprietary helical flow geometry. Helical flow is established by employing a rifled groove machined into the cylindrical inner wall of the stainless steel housing and by placing the input and output liquid fittings tangent to this wall. Fluid flowing into the cell is directed at the cell wall rather than at the internal reflectance sensing element. This factor, combined with the rifling, forces it to follow a helical path, spiraling around the element before exiting the cell.

The helical path provides a number of benefits. First, the input flow offset, combined with the centrifugal effect due to the spiraling action, minimizes any abrasion of the sensing element due to particulate matter which may be included in the flow. Secondly, the helical path forces the fluid to reach every por-

tion of the cell volume while at the same time traveling at a much greater velocity than it would if it were to follow the most direct path to the output orifice. This eliminates dead volume and the associated sample retention and assures that the cell will be thoroughly and rapidly cleaned out when flushed with a solvent. Highly viscous samples such as toothpaste can be analyzed and then completely flushed out in a just few seconds.

## STANDARD TUNNEL CELLS

### Model Number Designations

TUNNEL Cell models are specified by a combination of a three digit model number (120, 130, and 131) and one or more suffixes. The basic model number gives an indication of the element size and approximate sample volume. Micro TUNNEL Cells (TNL-120) use a 1/8" diameter element and have sample volumes in the range of 25 to 50ul. Models TNL-130 and TNL-131 use 1/4" diameter elements and have approximate volumes of 2ml and 20ml respectively. Letter suffixes indicate individual cell structures.

Number suffixes are used to indicate the internal reflectance element material. These are listed on the last page. If no number is specified, the element material is assumed to be ZnSe.

### Integrated Temperature Control

TUNNEL Cell models having the suffixes C and H feature temperature control capability integrated into the cell structure. No separate heating or cooling jacket is required. The "C" version includes a temperature control liquid flow channel which traverses all four edges of the square cross-section cell. It is designed to be used with any of the common circulating baths.

Models with the suffix "H" include a cartridge heater and a thermocouple sensor mounted adjacent to the sample chamber. They can be used with a wide range of temperature controllers such as the Omega CN9111. When used with Model TNH-301 Insulating Jacket, these models can be operated at temperatures as high as 230°C.

### High Pressure Operation

The mechanical designs of all of the TUNNEL Cells are compatible with operation at pressures to 1500 PSI. However, individual internal reflectance elements may not tolerate this full range. If your application requires operation at elevated pressures, please inquire with Axiom regarding pretesting to insure that the element delivered with your cell is compatible with your anticipated range of operating pressures.

## INDUSTRIAL SYSTEM CONFIGURATIONS

### Outboard Operation

All TUNNEL Cell models can be interfaced to the AXIOT™ System of optical transfer modules. As a result, these cells can be operated outside of the FTIR sample compartment as long as the spectrometer is provided with a output beam port. This mode of operation is especially important for on-line applications in which it is not practical to pipe the sample to the spectrometer. Instead, the use of the AXIOT System allows the beam from the spectrometer to be transmitted to the sample. In the laboratory, out-board operation leaves the sample compartment free for other tasks and eliminates the possibility of instrument damage due to a chemical spill in the sample compartment.

The AXIOT System can be used to transfer the FTIR beam for distances of ten to twenty feet with minimal signal loss. AXIOT elements are fully purgeable and in most situations, require no adjustment.

### Integrated Quality Control Configurations

The use of modular AXIOT components allows the easy configuration of a wide variety of TUNNEL optical systems for specialized applications. In addition, these systems can be combined with on-the-shelf temperature control, switching, and pumping equipment to provide integrated systems for quality control functions such as incoming inspection, final test, or near-line process sampling. Axiom is prepared to quote on such dedicated systems to meet any of your QC needs.

### On-line Process Monitoring

Rugged, adjustment-free construction and a high degree of measurement accuracy make the entire TUNNEL Cell line compatible with on-line process applications. However, some models are uniquely suited for particular applications. One example is Model TNL-131H. Its relatively large flow volume combined with the helical flow geometry and integral cartridge heating makes it ideally suited for monitoring continuous processes involving either viscous fluids or high flow rates.

In many pilot plant processes, sample volumes are quite small. Such processes can be monitored by using a Model TNL-120A Micro TUNNEL Cell. When the process is subsequently scaled up, the monitoring system can also be scaled up to use a larger volume cell.

In addition to the TUNNEL Cells, Axiom has developed a line of "Deep Immersion Probes" for the in-situ monitoring of batch reactions either in the laboratory or in a manufacturing process. These devices use the same optical principles as the TUNNEL Cells. As a result, the chemistry of a given process can often be modeled by using data taken with a TUNNEL Cell before proceeding to in-situ monitoring using a probe. The Deep Immersion Probe product line is described in Axiom data sheet PS-DPR-01. Performance data is provided in Technical Note AN-903[4].

## STANDARD TUNNEL CELL MODELS

The model designations below include a suffix of the form x,y, where "x" indicates the housing option and "y" indicates the ATR element material. Standard materials are:

y = 1: ZnSe
y = 2: AMTIR
y = 3: ZnS

### TNL-120x,y Micro TUNNEL Cell

- Element dimensions (dia. x length): 0.125" x 1.625"
- Number of effective refections: 10
- Optical aperture: 0.3" diameter
- Housing options:
  - x = A: Standard rifled housing (40ul)
  - x = B: Open boat (50ul)
  - x = L: Capillary HPLC design (25ul)

---

### TNL-130x,y Standard TUNNEL Cell

- Element dimensions (dia. x length): 0.25" x 3.25"
- Number of effective reflections: 11
- Optical aperture: 0.6" diameter
- Housing options: (all 2ml volume)
  - x = A: Standard rifled housing
  - x = B: Open boat
  - x = C: Circulating liquid temperature control
  - x = H: Cartridge heater and thermocouple (for use with a commercial temperature controller)

---

### TNL-131x,y High Volume TUNNEL Cell

- Element dimensions (dia. x length): 0.25" x 3.25"
- Number of effective reflections: 11
- Optical aperature: 0.6" diameter
- Housing options: (all 20ml volume)
  - x = A: Standard rifled housing
  - x = C: Circulating liquid temperature control
  - x = H: Cartridge heater and thermocouple (for use with a commercial temperature controller)

**References:**


1. E. H. Braue, Jr. and M. G. Pannela, Applied Spectroscopy, 41, 1057 (1987).
2. Tomas Hirschfeld in Fourier Transform Infrared Spectroscopy, Vol. 2, ed. J. R. Ferraro & L. J. Basile, Academic Press, New York, 1979, pp. 215-221.
3. W. M. Doyle, "Absorbance Linearity and Repeatability In Cylindrical Internal Reflectance FT-IR Spectroscopy of Liquids", (To be published in Applied Spectroscopy).
4. W. M. Doyle and N. A. Jennings, "FT-IR Chemical Reaction Monitoring Using An In-situ Deep Immersion Probe", (To be published in Spectroscopy).

Axiom Analytical INCORPORATED

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Tel. (714) 497-1407
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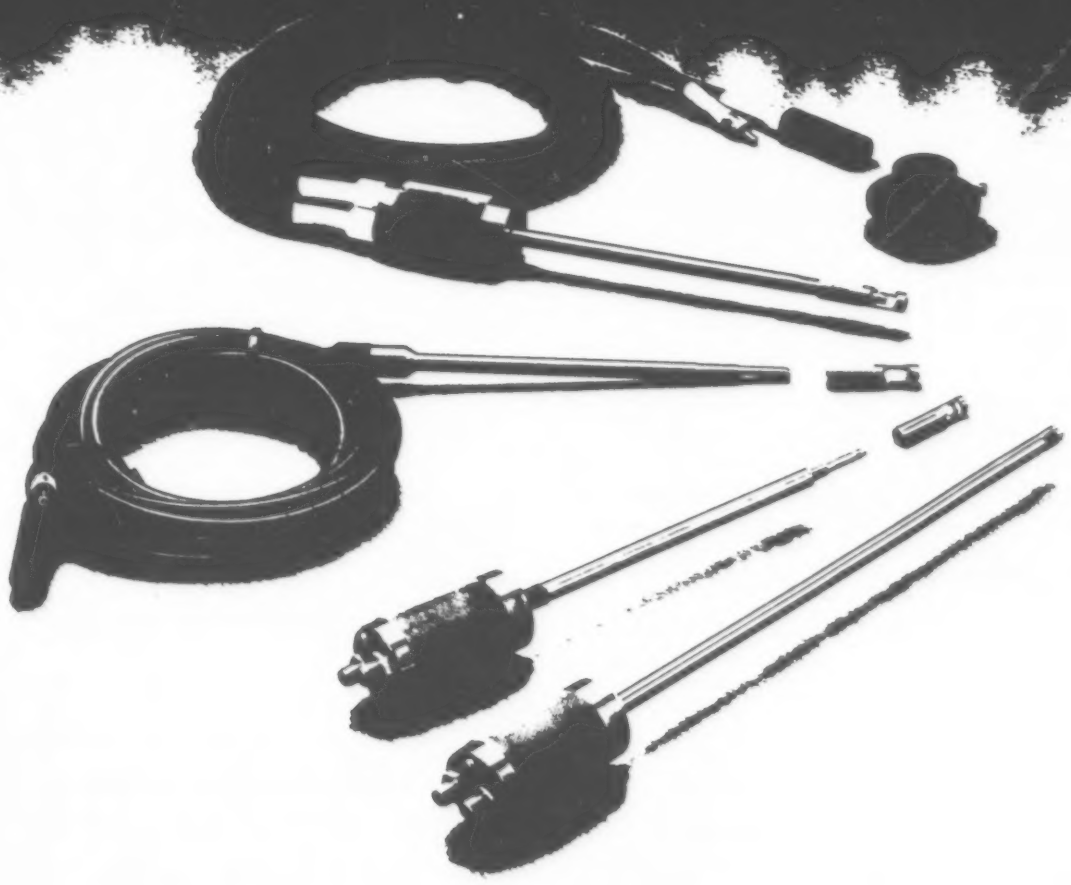
# APPENDIX G

Wand Probe Product Information

# WAND PROBES

- For Transmission, Reflectance or Fluorescence
- Easy to Use and Install
- Ideal for Laboratory and Process Applications
- Single Strand and Bundle Types



**Wand (or dip type) Probes are single sided probes for optical transmission, absorbance, reflectance and fluorescence measurements that can be used in laboratory reactors, in process lines, or in a laboratory bench setting.**

**Designed in single strand fiber and fiber bundle configurations, the wand probe employs a mirrored tip to reflect light from the sending fiber(s) to the receiving fiber(s). The absorbance tips are available in a variety of materials and path lengths. Without the tips, the fiber bundle probes can be used for reflectance and fluorescence measurements.**

| | |
|---|---|
| Body material | 316 SS (Others, e.g. Hastelloy and Monel, are available on special order.) |
| Mirror material | Gold, rhodium on brass, or rhodium on gold |
| Seal | Epoxy seal to fiber body |
| Items contacting sample | Body/mirror material, epoxy, silica |
| Optics | Mirror focuses light back to fiber(s) |
| Path length range | Selected lengths from 5 to 30 mm for single strand probes, 10 to 30 mm for bundle probes, and 1 to 10 mm variable for bundle probes |
| Temperature/pressure | 0-200°C/0-1000 psi (69 bar). Very dependent on sample matrix. |

## ORDERING INFORMATION

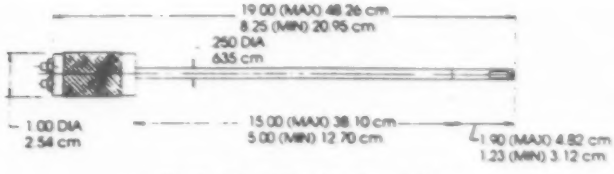
### Single Wand Fiber probes

General Description: 316 SS probe body, 0.25" (6.4 mm) OD shaft. Two female SMA connectors provided for termination of sending and receiving fiber. Probe internally contains two single strand fibers. Mirror tip and fiber optic cables must be ordered separately. Accepts WTS series mirrored tips.

Part Number
1-1WX S O - X X

- Diameter of fiber
  Leave blank for 320 micron core
  Enter B for 500 micron core
- Length of probe
  Enter 5 for 5.5" (139.7 mm)
  Enter 8 for 8.5" (215.9 mm)
- Type of fiber
  Enter 2 for UV-VIS 250-800 nm
  Enter 4 for VIS-NIR 400-2100 nm

Example: 1-1WZS 0-5 is a UV-VIS 5.5" wand probe with 320 micron fiber and female SMA connectors on input and output sides.




**Single Fiber Wand Probe and Tip**

### Absorbance/Reflective Tips With Mirrors

General Description: Tip screws on to the end of wand type probes. Tip is 316 SS and has mirror bonded to it.

Part Number
WT X X - X

- Type of mirror
  Enter R for rhodium on brass
  Enter AU for gold (NIR only)
  Enter AUR for rhodium plated gold
- Enter path length as 5 *, 10, 20, or 30 ** mm
  or V ** for variable path (1 to 10 mm)
- Enter B for bundle fiber probe
  Enter S for single fiber probe

* Only available for single fiber (S type) probes
** Only available for bundle fiber (B type) probes
Note: WTS tips are 0.25" (6.35 mm) OD
WTB tips are 0.312" (7.92 mm) OD

### Bundle Fiber Wand Probes

General Description: 316 SS probe body, 0.25" (6.4 mm) OD shaft (approx. 5.5" (140 mm) long for 6 to 1 and 5" (127 mm) long for others). Fiber cable is 0.25" (6.4 mm) OD aluminum monocoil with PVC jacket and contains multiple strands of fiber. Input side is terminated in an SMA connector. Output side is terminated in an in-line slit bundle connector (PA200 bundle port adapter required) or an SMA connector. Accepts WTB series mirrored tips.

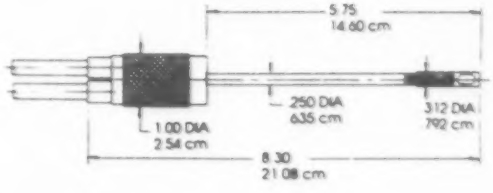
Part Number

| | |
|---|---|
| 6-1 WX X X - 6 | 6 receiving fibers, 1 sending |
| 7-7 WX X X - S | 7 receiving fibers, 7 sending |
| 10-9 WX X X - S | 10 receiving fibers, 9 sending |

- Enter fiber length in meters
  Min: 2 M, Max 6 M (must be integer)
- Type of termination
  Enter S for SMA on input and output side
  Enter B for SMA on input side and bundle connector on output side (normal usage)
- Type of fiber
  Enter 2 for UV-VIS 250-800 nm
  Enter 4 for VIS-NIR 400-2100 nm

Example: 7-7 W4B2-S is a VIS-NIR probe with an SMA connector on the input side and a bundle connector on the output side. Fiber cable is 2 meters long.

Standard probes have two or six meters fiber optic cable. Other lengths are available on special order.




**6:1 Bundle Fiber Wand Probe and Tip**

### Accessories (pictured)

Part Number

| | |
|---|---|
| PA200 | Bundle port adapter 0.5" (12.7 mm) diameter bore for use with bundle probes |

Specifications subject to change without notice. User takes full responsibility that probes are compatible with physical (temperature and pressure) and chemical make up of sample. Drawings are not to scale.

# GUIDED WAVE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